Pearson New International Edition

Inorganic Chemistry

Gary L. Miessler Paul J. Fischer
Donald A. Tarr

Fifth Edition

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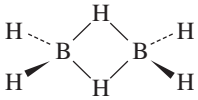
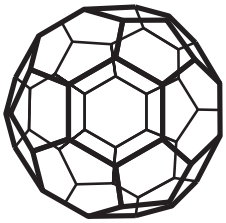


Introduction to Inorganic Chemistry



1 What Is Inorganic Chemistry?

If organic chemistry is defined as the chemistry of hydrocarbon compounds and their derivatives, inorganic chemistry can be described broadly as the chemistry of "everything else." This includes all the remaining elements in the periodic table, as well as carbon, which plays a major and growing role in inorganic chemistry. The large field of organometallic chemistry bridges both areas by considering compounds containing metal–carbon bonds; it also includes catalysis of many organic reactions. Bioinorganic chemistry bridges biochemistry and inorganic chemistry and has an important focus on medical applications. Environmental chemistry includes the study of both inorganic and organic compounds. In short, the inorganic realm is vast, providing essentially limitless areas for investigation and potential practical applications.

2 Contrasts with Organic Chemistry

Some comparisons between organic and inorganic compounds are in order. In both areas, single, double, and triple covalent bonds are found (**Figure 1**); for inorganic compounds, these include direct metal—metal bonds and metal—carbon bonds. Although the maximum number of bonds between two carbon atoms is three, there are many compounds that contain quadruple bonds between metal atoms. In addition to the sigma and pi bonds common in organic chemistry, quadruply bonded metal atoms contain a delta (δ) bond (**Figure 2**); a combination of one sigma bond, two pi bonds, and one delta bond makes up the quadruple bond. The delta bond is possible in these cases because the metal atoms have *d* orbitals to use in bonding, whereas carbon has only *s* and *p* orbitals energetically accessible for bonding.

Compounds with "fivefold" bonds between transition metals have been reported (**Figure 3**), accompanied by debate as to whether these bonds merit the designation "quintuple."

In organic compounds, hydrogen is nearly always bonded to a single carbon. In inorganic compounds, hydrogen is frequently encountered as a bridging atom between two or more other atoms. Bridging hydrogen atoms can also occur in metal cluster compounds, in which hydrogen atoms form bridges across edges or faces of polyhedra of metal atoms. Alkyl groups may also act as bridges in inorganic compounds, a function rarely encountered in organic chemistry except in reaction intermediates. Examples of terminal and bridging hydrogen atoms and alkyl groups in inorganic compounds are in **Figure 4**.

Some of the most striking differences between the chemistry of carbon and that of many other elements are in coordination number and geometry. Although carbon is usually limited to a maximum coordination number of four (a maximum of four atoms bonded

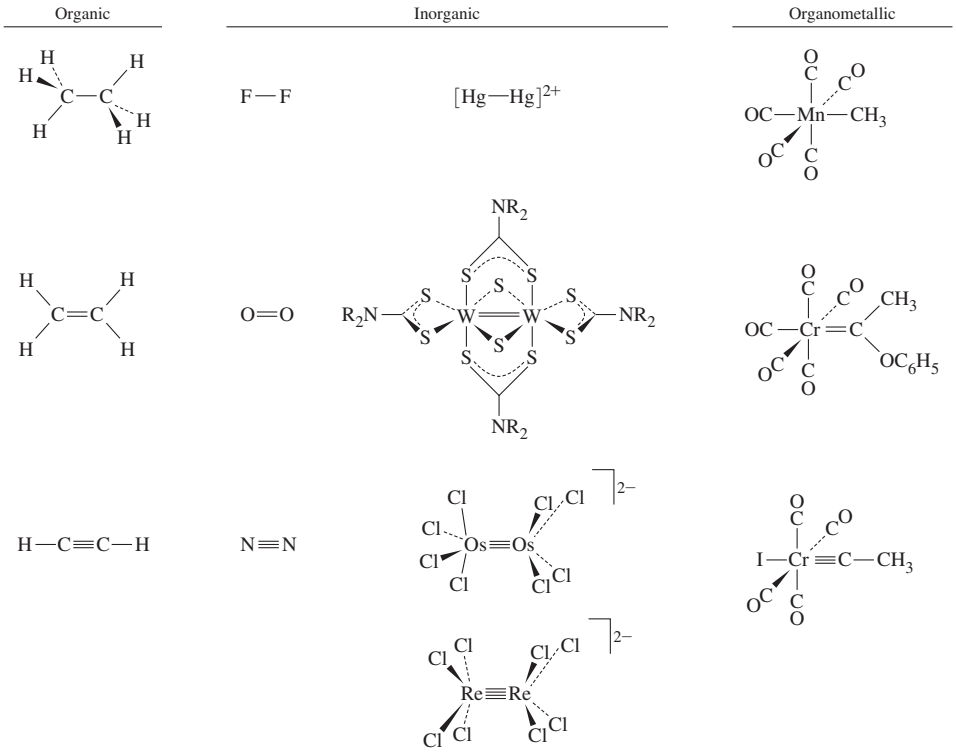


FIGURE 1 Single and Multiple Bonds in Organic and Inorganic Molecules.

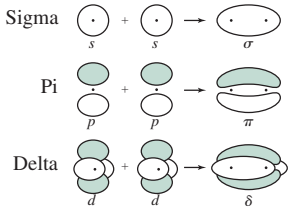


FIGURE 2 Examples of Bonding Interactions.

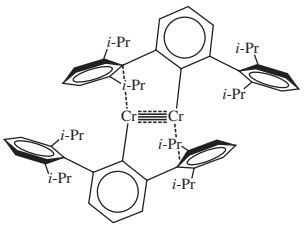


FIGURE 3 Example of Fivefold Bonding.

to carbon, as in CH_4), numerous inorganic compounds have central atoms with coordination numbers of five, six, seven, and higher; the most common coordination geometry for transition metals is an octahedral arrangement around a central atom, as shown for $[TiF_6]^{3-}$ (**Figure 5**). Furthermore, inorganic compounds present coordination geometries different from those found for carbon. For example, although 4-coordinate carbon is nearly always tetrahedral, both tetrahedral and square-planar shapes occur for 4-coordinate compounds of both metals and nonmetals. When metals are in the center, with anions or neutral molecules (*ligands*) bonded to them (frequently through N, O, or S), these are called *coordination complexes*; when carbon is the element directly bonded to metal atoms or ions, they are also classified as *organometallic* complexes.

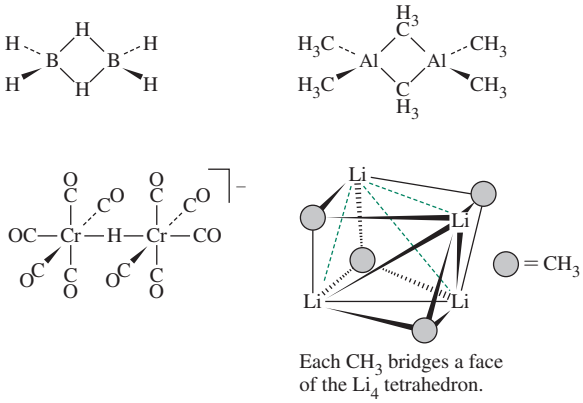


FIGURE 4 Examples of Inorganic Compounds Containing Terminal and Bridging Hydrogens and Alkyl Groups.

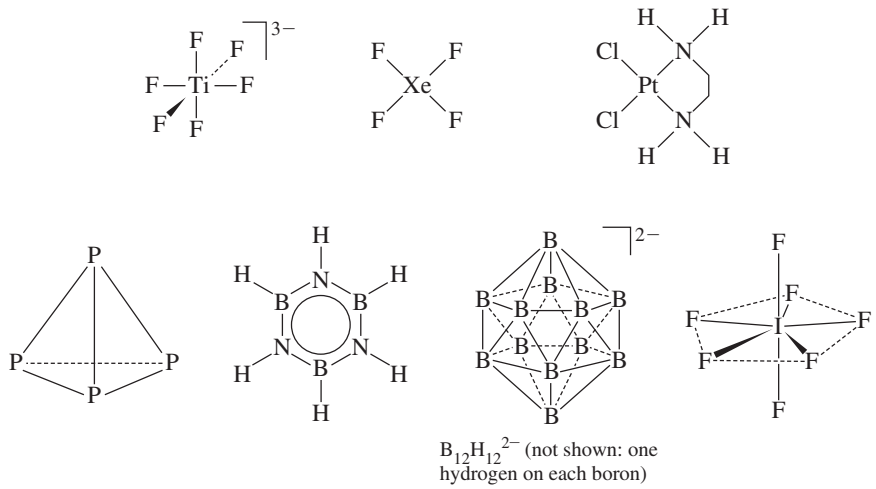


FIGURE 5 Examples of Geometries of Inorganic Compounds.

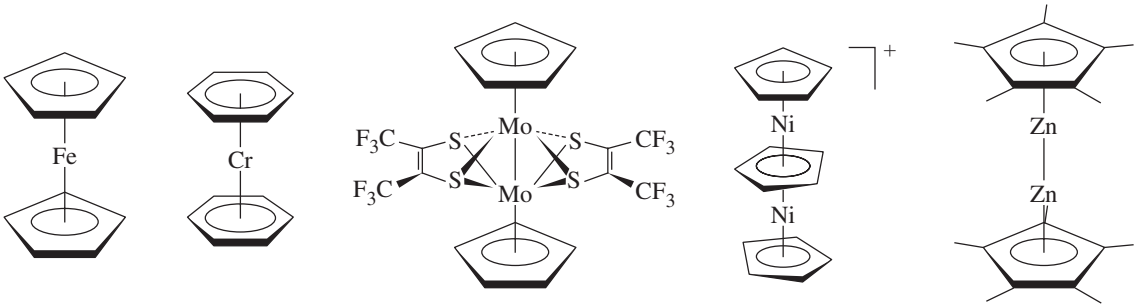


FIGURE 6 Inorganic Compounds Containing Pi-Bonded Aromatic Rings.

The tetrahedral geometry usually found in 4-coordinate compounds of carbon also occurs in a different form in some inorganic molecules. Methane contains four hydrogens in a regular tetrahedron around carbon. Elemental phosphorus is tetratomic (P_4) and tetrahedral, but with no central atom. Other elements can also form molecules in which outer atoms surround a central cavity; an example is boron, which forms numerous structures containing icosahedral B_{12} units. Examples of some of the geometries found for inorganic compounds are in Figure 5.

Aromatic rings are common in organic chemistry, and aryl groups can also form sigma bonds to metals. However, aromatic rings can also bond to metals in a dramatically different fashion using their pi orbitals, as shown in **Figure 6**. The result is a metal atom bonded above the center of the ring, almost as if suspended in space. In many cases, metal atoms are sandwiched between two aromatic rings. Multiple-decker sandwiches of metals and aromatic rings are also known.

Carbon plays an unusual role in a number of metal *cluster compounds* in which a carbon atom is at the center of a polyhedron of metal atoms. Examples of carbon-centered clusters with five, six, or more surrounding metals are known (**Figure 7**). The striking role that carbon plays in these clusters has provided a challenge to theoretical inorganic chemists.

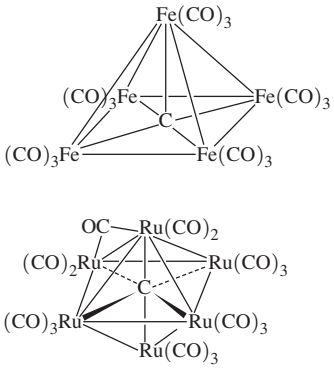


FIGURE 7 Carbon-Centered Metal Clusters.

In addition, since the mid-1980s the chemistry of elemental carbon has flourished. This phenomenon began with the discovery of fullerenes, most notably the cluster C_{60}, dubbed "buckminsterfullerene" after the developer of the geodesic dome. Many other fullerenes (buckyballs) are now known and serve as cores of a variety of derivatives. In

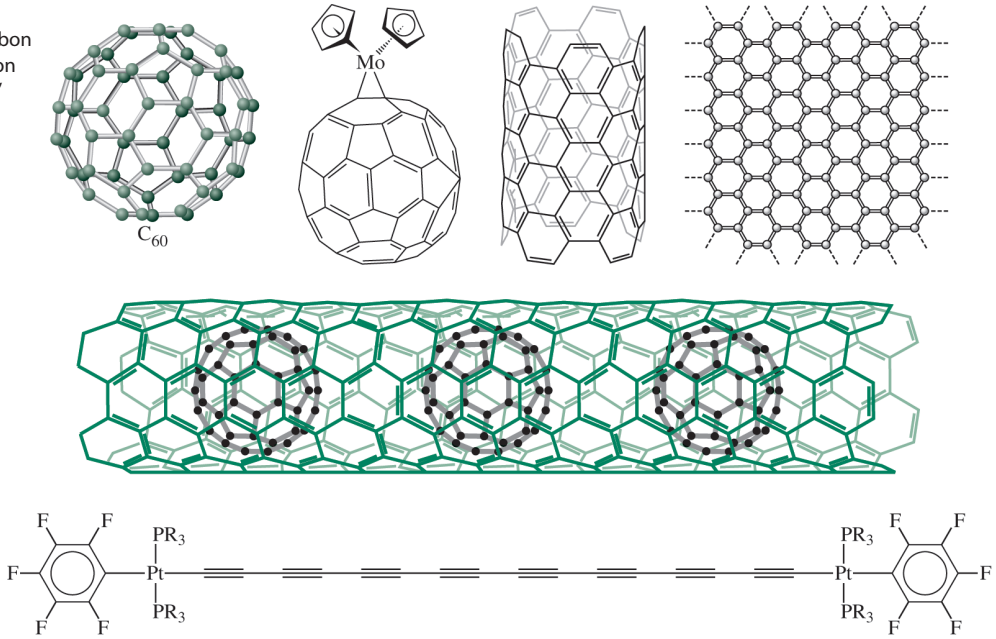


FIGURE 8 The Fullerene C_{60}, a Fullerene Compound, a Carbon Nanotube, Graphene, a Carbon Peapod, and a Polyyne "Wire" Connecting Platinum Atoms.

addition, numerous other forms of carbon (for example, carbon nanotubes, nanoribbons, graphene, and carbon wires) have attracted much interest and show potential for applications in fields as diverse as nanoelectronics, body armor, and drug delivery. **Figure 8** provides examples of these newer forms of carbon.

The era of sharp dividing lines between subfields in chemistry has long been obsolete. Many of the subjects in this text, such as acid–base chemistry and organometallic reactions, are of vital interest to organic chemists. Other topics such as oxidation–reduction reactions, spectra, and solubility relations interest analytical chemists. Subjects related to structure determination, spectra, conductivity, and theories of bonding appeal to physical chemists. Finally, the use of organometallic catalysts provides a connection to petroleum and polymer chemistry, and coordination compounds such as hemoglobin and metal-containing enzymes provide a similar tie to biochemistry. Many inorganic chemists work with professionals in other fields to apply chemical discoveries to addressing modern challenges in medicine, energy, the environment, materials science, and other fields. In brief, modern inorganic chemistry is not a fragmented field of study, but has numerous interconnections with other fields of science, medicine, technology, and other disciplines.

The remainder of this chapter is devoted to a short history of the origins of inorganic chemistry and perspective on more recent developments, intended to provide a sense of connection to the past and to place some aspects of inorganic chemistry within the context of larger historical events.

3 The History of Inorganic Chemistry

Even before alchemy became a subject of study, many chemical reactions were used and their products applied to daily life. The first metals used were probably gold and copper, which can be found in the metallic state in nature. Copper can also be readily formed by the reduction of malachite—basic copper carbonate, $Cu_2(CO_3)(OH)_2$—in charcoal fires. Silver, tin, antimony, and lead were also known as early as 3000 BCE. Iron appeared in

classical Greece and in other areas around the Mediterranean Sea by 1500 BCE. At about the same time, colored glasses and ceramic glazes were introduced, largely composed of silicon dioxide (SiO_2, the major component of sand) and other metallic oxides, which had been melted and allowed to cool to amorphous solids.

Alchemists were active in China, Egypt, and other centers of civilization early in the first centuries CE. Although much effort went into attempts to "transmute" base metals into gold, alchemists also described many other chemical reactions and operations. Distillation, sublimation, crystallization, and other techniques were developed and used in their studies. Because of the political and social changes of the time, alchemy shifted into the Arab world and later—about 1000 to 1500 CE—reappeared in Europe. Gunpowder was used in Chinese fireworks as early as 1150, and alchemy was also widespread in China and India at that time. Alchemists appeared in art, literature, and science until at least 1600, by which time chemistry was beginning to take shape as a science. Roger Bacon (1214–1294), recognized as one of the first great experimental scientists, also wrote extensively about alchemy.

By the seventeenth century, the common strong acids—nitric, sulfuric, and hydrochloric—were known, and systematic descriptions of common salts and their reactions were being accumulated. As experimental techniques improved, the quantitative study of chemical reactions and the properties of gases became more common, atomic and molecular weights were determined more accurately, and the groundwork was laid for what later became the periodic table of the elements. By 1869, the concepts of atoms and molecules were well established, and it was possible for Mendeleev and Meyer to propose different forms of the periodic table. **Figure 9** illustrates Mendeleev's original periodic table.*

The chemical industry, which had been in existence since very early times in the form of factories for purifying salts and for smelting and refining metals, expanded as methods for preparing relatively pure materials became common. In 1896, Becquerel discovered radioactivity, and another area of study was opened. Studies of subatomic particles, spectra, and electricity led to the atomic theory of Bohr in 1913, which was soon modified by the quantum mechanics of Schrödinger and Heisenberg in 1926 and 1927.

Inorganic chemistry as a field of study was extremely important during the early years of the exploration and development of mineral resources. Qualitative analysis methods were

			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 53	Rh = 104.4	Pt = 197.4
			Fe = 56	Ru = 104.2	Ir = 198
			Ni = Co = 59	Pd = 106.6	Os = 199
H = 1			Cu = 63.4	Ag = 108	Hg = 200
	Be = 9.4	Mg = 24	Zn = 65.2	Cd = 112	
	B = 11	Al = 27.4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79.4	Te = 128?	
	F = 19	Cl = 35.5	Br = 80	J = 127	
Li = 7	Na = 23	K = 39	Rb = 85.4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87.6	Ba = 137	Pb = 207
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75.6	Th = 118 ?		

FIGURE 9 Mendeleev's 1869 Periodic Table. Two years later, Mendeleev revised his table into a form similar to a modern short-form periodic table, with eight groups across.

*The original table was published in *Zeitschrift für Chemie*, **1869**, *12*, 405. It can be found in English translation, together with a page from the German article, at web.lemoyne.edu/~giunta/mendeleev.html. See M. Laing, *J. Chem. Educ.*, **2008**, *85*, 63 for illustrations of Mendeleev's various versions of the periodic table, including his handwritten draft of the 1869 table.

developed to help identify minerals and, combined with quantitative methods, to assess their purity and value. As the Industrial Revolution progressed, so did the chemical industry. By the early twentieth century, plants for the high volume production of ammonia, nitric acid, sulfuric acid, sodium hydroxide, and many other inorganic chemicals were common.

Early in the twentieth century, Werner and Jørgensen made considerable progress on understanding the coordination chemistry of transition metals and also discovered a number of organometallic compounds. Nevertheless, the popularity of inorganic chemistry as a field of study gradually declined during most of the first half of the century. The need for inorganic chemists to work on military projects during World War II rejuvenated interest in the field. As work was done on many projects (not least of which was the Manhattan Project, in which scientists developed the fission bomb), new areas of research appeared, and new theories were proposed that prompted further experimental work. A great expansion of inorganic chemistry began in the 1940s, sparked by the enthusiasm and ideas generated during World War II.

In the 1950s, an earlier method used to describe the spectra of metal ions surrounded by negatively charged ions in crystals (**crystal field theory**)[1] was extended by the use of molecular orbital theory[2] to develop **ligand field theory** for use in coordination compounds, in which metal ions are surrounded by ions or molecules that donate electron pairs. This theory gave a more complete picture of the bonding in these compounds. The field developed rapidly as a result of this theoretical framework, availability of new instruments, and the generally reawakened interest in inorganic chemistry.

In 1955, Ziegler[3] and Natta[4] discovered organometallic compounds that could catalyze the polymerization of ethylene at lower temperatures and pressures than the common industrial method at that time. In addition, the polyethylene formed was more likely to be made up of linear, rather than branched, molecules and, as a consequence, was stronger and more durable. Other catalysts were soon developed, and their study contributed to the rapid expansion of organometallic chemistry, still a rapidly growing area.

The study of biological materials containing metal atoms has also progressed rapidly. The development of new experimental methods allowed more thorough study of these compounds, and the related theoretical work provided connections to other areas of study. Attempts to make *model* compounds that have chemical and biological activity similar to the natural compounds have also led to many new synthetic techniques. Two of the many biological molecules that contain metals are in **Figure 10**. Although these molecules have very different roles, they share similar ring systems.

One current area that bridges organometallic chemistry and bioinorganic chemistry is the conversion of nitrogen to ammonia:

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

This reaction is one of the most important industrial processes, with over 100 million tons of ammonia produced annually worldwide, primarily for fertilizer. However, in spite of metal oxide catalysts introduced in the Haber–Bosch process in 1913, and improved since then, it is also a reaction that requires temperatures between 350 and 550 °C and from 150–350 atm pressure and that still results in a yield of only 15 percent ammonia. Bacteria, however, manage to fix nitrogen (convert it to ammonia and then to nitrite and nitrate) at 0.8 atm at room temperature in nodules on the roots of legumes. The nitrogenase enzyme that catalyzes this reaction is a complex iron–molybdenum–sulfur protein. The structure of its active sites has been determined by X-ray crystallography.[5] A vigorous area of modern inorganic research is to design reactions that could be carried out on an industrial scale that model the reaction of nitrogenase to generate ammonia under mild conditions. It is estimated that as much as 1 percent of the world's total energy consumption is currently used for the Haber–Bosch process.

Inorganic chemistry also has medical applications. Notable among these is the development of platinum-containing antitumor agents, the first of which was the *cis* isomer of $Pt(NH_3)_2Cl_2$,

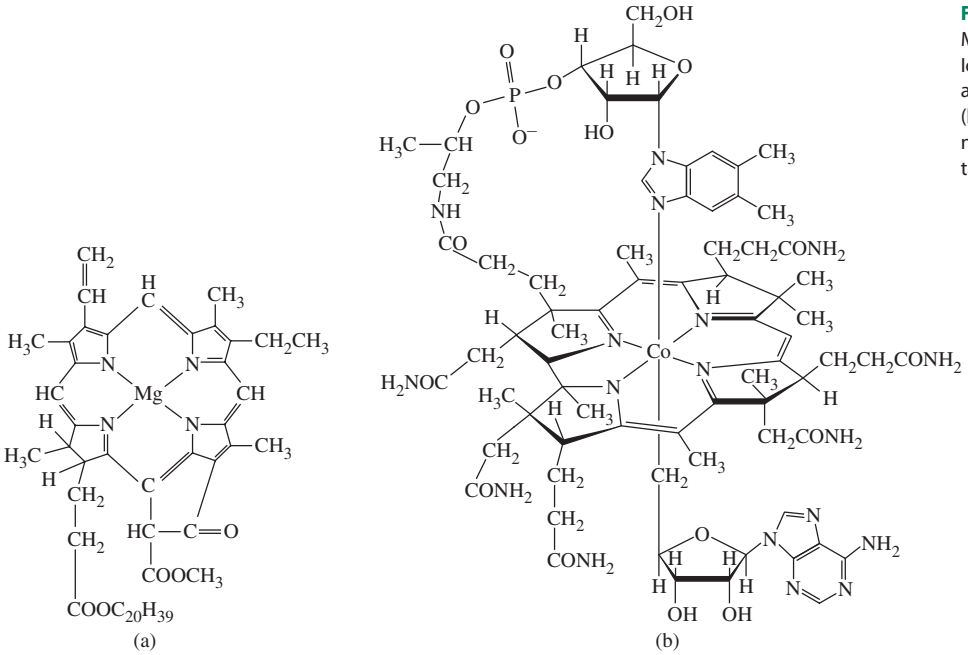


FIGURE 10 Biological Molecules Containing Metal Ions. (a) Chlorophyll a, the active agent in photosynthesis. (b) Vitamin B_{12} coenzyme, a naturally occurring organometallic compound.

cisplatin. First approved for clinical use approximately 30 years ago, cisplatin has served as the prototype for a variety of anticancer agents; for example, satraplatin, the first orally available platinum anticancer drug to reach clinical trials.* These two compounds are in **Figure 11**.

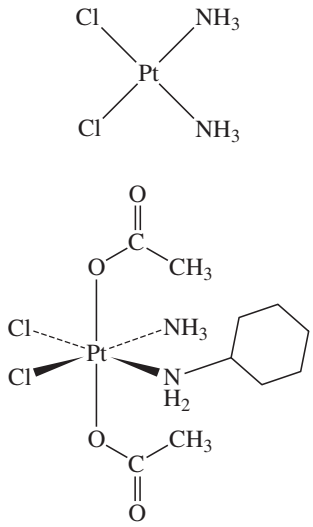


FIGURE 11 Cisplatin and Satraplatin.

4 Perspective

The premier issue of the journal *Inorganic Chemistry*** was published in February 1962. Much of the focus of that issue was on classic coordination chemistry, with more than half its research papers on synthesis of coordination complexes and their structures and properties. A few papers were on compounds of nonmetals and on organometallic chemistry, then a relatively new field; several were on thermodynamics or spectroscopy. All of these topics have developed considerably in the subsequent half-century, but much of the evolution of inorganic chemistry has been into realms unforeseen in 1962.

The 1962 publication of the first edition of F. A. Cotton and G. Wilkinson's landmark text *Advanced Inorganic Chemistry*[6] provides a convenient reference point for the status of inorganic chemistry at that time. For example, this text cited only the two long-known forms of carbon, diamond and graphite, although it did mention "amorphous forms" attributed to microcrystalline graphite. It would not be until more than two decades later that carbon chemistry would explode with the seminal discovery of C_{60} in 1985 by Kroto, Curl, Smalley, and colleagues,[7] followed by other fullerenes, nanotubes, graphene, and other forms of carbon (Figure 8) with the potential to have major impacts on electronics, materials science, medicine, and other realms of science and technology.

As another example, at the beginning of 1962 the elements helium through radon were commonly dubbed "inert" gases, believed to "form no chemically bound compounds" because of the stability of their electron configurations. Later that same year, Bartlett

*For reviews of modes of interaction of cisplatin and related drugs, see P. C. A. Bruijnincx, P. J. Sadler, *Curr. Opin. Chem. Bio.*, **2008**, *12*, 197 and F. Arnesano, G. Natile, *Coord. Chem. Rev.*, **2009**, *253*, 2070.

**The authors of this issue of *Inorganic Chemistry* were a distinguished group, including five recipients of the Priestley Medal, the highest honor conferred by the American Chemical Society, and 1983 Nobel Laureate Henry Taube.

reported the first chemical reactions of xenon with PtF_6, launching the synthetic chemistry of the now-renamed "noble" gas elements, especially xenon and krypton;[8] numerous compounds of these elements have been prepared in succeeding decades.

Numerous square planar platinum complexes were known by 1962; the chemistry of platinum compounds had been underway for more than a century. However, it was not known until Rosenberg's work in the latter part of the 1960s that one of these, *cis*-$Pt(NH_3)_2Cl_2$ (cisplatin, Figure 11), had anticancer activity.[9] Antitumor agents containing platinum and other transition metals have subsequently become major tools in treatment regimens for many types of cancer.[10]

That first issue of *Inorganic Chemistry* contained only 188 pages, and the journal was published quarterly, exclusively in hardcopy. Researchers from only four countries were represented, more than 90 percent from the United States, the others from Europe. *Inorganic Chemistry* now averages approximately 550 pages per issue, is published 24 times annually, and publishes (electronically) research conducted broadly around the globe. The growth and diversity of research published in *Inorganic Chemistry* has been paralleled in a wide variety of other journals that publish articles on inorganic and related fields.

In the preface to the first edition of *Advanced Inorganic Chemistry*, Cotton and Wilkinson stated, "in recent years, inorganic chemistry has experienced an impressive renaissance." This renaissance shows no sign of diminishing.

With this brief survey of the marvelously complex field of inorganic chemistry, we now turn to the details in the remainder of this text. The topics included provide a broad introduction to the field. However, even a cursory examination of a chemical library or one of the many inorganic journals shows some important aspects of inorganic chemistry that must be omitted in a textbook of moderate length. The references cited in this text suggest resources for further study, including historical sources, texts, and reference works that provide useful additional material.

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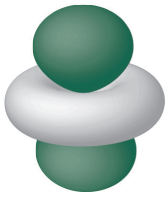
General References

For those who are interested in the historical development of inorganic chemistry focused on metal coordination compounds during the period 1798–1935, copies of key research papers, including translations, are provided in the three-volume set *Classics in Coordination Chemistry*, G. B. Kauffman, ed., Dover Publications, N.Y. 1968, 1976, 1978. Among the many general reference works available, three of the most useful and complete are N. N. Greenwood and A. Earnshaw's *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford, 1997; F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochman's *Advanced Inorganic Chemistry*, 6th ed., John Wiley & Sons, New York, 1999; and A. F. Wells's *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, New York, 1984. An interesting study of inorganic reactions from a different perspective can be found in G. Wulfsberg's *Principles of Descriptive Inorganic Chemistry*, Brooks/Cole, Belmont, CA, 1987.

Atomic Structure



Understanding the structure of the atom has been a fundamental challenge for centuries. It is possible to gain a practical understanding of atomic and molecular structure using only a moderate amount of mathematics rather than the mathematical sophistication of quantum mechanics. This chapter introduces the fundamentals needed to explain atomic structure in qualitative and semiquantitative terms.

1 Historical Development of Atomic Theory

Although the Greek philosophers Democritus (460–370 BCE) and Epicurus (341–270 BCE) presented views of nature that included atoms, many centuries passed before experimental studies could establish the quantitative relationships needed for a coherent atomic theory. In 1808, John Dalton published *A New System of Chemical Philosophy*,[1] in which he proposed that

> … the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc. In other words, every particle of water is like every other particle of water; every particle of hydrogen is like every other particle of hydrogen, etc.[2]

and that atoms combine in simple numerical ratios to form compounds. The terminology he used has since been modified, but he clearly presented the concepts of atoms and molecules, and made quantitative observations of the masses and volumes of substances as they combined to form new substances. For example, in describing the reaction between the gases hydrogen and oxygen to form water Dalton said that

> When two measures of hydrogen and one of oxygen gas are mixed, and fired by the electric spark, the whole is converted into steam, and if the pressure be great, this steam becomes water. It is most probable then that there is the same number of particles in two measures of hydrogen as in one of oxygen.[3]

Because Dalton was not aware of the diatomic nature of the molecules H_2 and O_2, which he assumed to be monatomic H and O, he did not find the correct formula of water, and therefore his surmise about the relative numbers of particles in "measures" of the gases is inconsistent with the modern concept of the mole and the chemical equation $2H_2 + O_2 \rightarrow 2H_2O$.

Only a few years later, Avogadro used data from Gay-Lussac to argue that equal volumes of gas at equal temperatures and pressures contain the same number of molecules, but uncertainties about the nature of sulfur, phosphorus, arsenic, and mercury vapors delayed acceptance of this idea. Widespread confusion about atomic weights and molecular formulas contributed to the delay; in 1861, Kekulé gave 19 different possible formulas for acetic acid![4] In the 1850s, Cannizzaro revived the argument of Avogadro and argued that

everyone should use the same set of atomic weights rather than the many different sets then being used. At a meeting in Karlsruhe in 1860, Cannizzaro distributed a pamphlet describing his views.[5] His proposal was eventually accepted, and a consistent set of atomic weights and formulas evolved. In 1869, Mendeleev[6] and Meyer[7] independently proposed periodic tables nearly like those used today, and from that time the development of atomic theory progressed rapidly.

1.1 The Periodic Table

The idea of arranging the elements into a periodic table had been considered by many chemists, but either data to support the idea were insufficient or the classification schemes were incomplete. Mendeleev and Meyer organized the elements in order of atomic weight and then identified groups of elements with similar properties. By arranging these groups in rows and columns, and by considering similarities in chemical behavior as well as atomic weight, Mendeleev found vacancies in the table and was able to predict the properties of several elements—gallium, scandium, germanium, and polonium—that had not yet been discovered. When his predictions proved accurate, the concept of a periodic table was quickly accepted. The discovery of additional elements not known in Mendeleev's time and the synthesis of heavy elements have led to the modern periodic table.

In the modern periodic table, a horizontal row of elements is called a **period** and a vertical column is a **group**. The traditional designations of groups in the United States differ from those used in Europe. The International Union of Pure and Applied Chemistry (IUPAC) has recommended that the groups be numbered 1 through 18. In this text, we will use primarily the IUPAC group numbers. Some sections of the periodic table have traditional names, as shown in **Figure 1**.

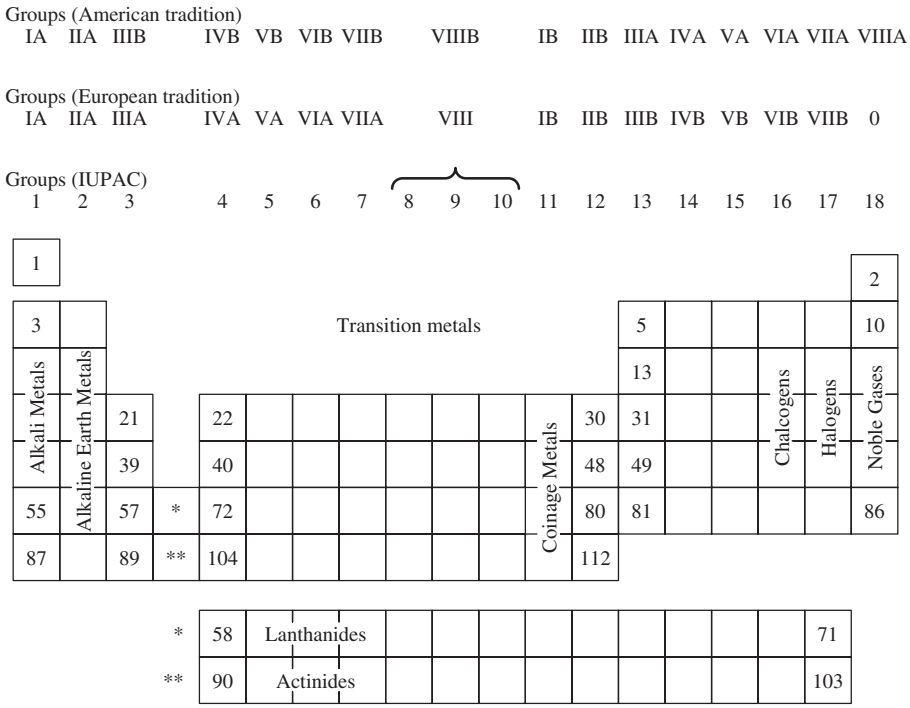


FIGURE 1 Numbering Schemes and Names for Parts of the Periodic Table.

1.2 Discovery of Subatomic Particles and the Bohr Atom

During the 50 years after the periodic tables of Mendeleev and Meyer were proposed, experimental advances came rapidly. Some of these discoveries are listed in **Table 1**.

Parallel discoveries in atomic spectra showed that each element emits light of specific energies when excited by an electric discharge or heat. In 1885, Balmer showed that the energies of visible light emitted by the hydrogen atom are given by the equation

$$E = R_H\left(\frac{1}{2^2} - \frac{1}{n_h^2}\right)$$

where n_h = integer, with $n_h > 2$

R_H = Rydberg constant for hydrogen

$= 1.097 \times 10^7\ \text{m}^{-1} = 2.179 \times 10^{-18}\ \text{J} = 13.61\ \text{eV}$

and the energy of the light emitted is related to the wavelength, frequency, and wavenumber of the light, as given by the equation

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

where h = Planck constant $= 6.626 \times 10^{-34}$ J s

ν = frequency of the light, in s^{-1}

c = speed of light $= 2.998 \times 10^8\ \text{m s}^{-1}$

λ = wavelength of the light, frequently in nm

$\bar{\nu}$ = wavenumber of the light, usually in cm^{-1}

In addition to emission of visible light, as described by the Balmer equation, infrared and ultraviolet emissions were also discovered in the spectrum of the hydrogen atom. The energies of these emissions could be described by replacing 2^2 by integers n_l^2 in Balmer's original equation, with the condition that $n_l < n_h$ (l for lower level, h for higher level). These quantities, n, are called **quantum numbers**. (These are the **principal quantum numbers**; other quantum numbers are discussed in **Section 2.2**.) The origin of this energy was unknown until Niels Bohr's quantum theory of the atom,[8] first published in 1913 and refined over the following decade. This theory assumed that negatively charged electrons in atoms move in stable circular orbits around the positively charged nucleus with no absorption or emission of energy. However, electrons may absorb light of certain specific energies

TABLE 1 Discoveries in Atomic Structure

1896	A. H. Becquerel	Discovered radioactivity of uranium
1897	J. J. Thomson	Showed that electrons have a negative charge, with charge/mass $= 1.76 \times 10^{11}$ C/kg
1909	R. A. Millikan	Measured the electronic charge as 1.60×10^{-19} C; therefore, mass of electron $= 9.11 \times 10^{-31}$ kg
1911	E. Rutherford	Established the nuclear model of the atom: a very small, heavy nucleus surrounded by mostly empty space
1913	H. G. J. Moseley	Determined nuclear charges by X-ray emission, establishing atomic numbers as more fundamental than atomic masses

and be excited to orbits of higher energy; they may also emit light of specific energies and fall to orbits of lower energy. The energy of the light emitted or absorbed can be found, according to the Bohr model of the hydrogen atom, from the equation

$$E = R\left(\frac{1}{n_l^2} - \frac{1}{n_h^2}\right)$$

where

$$R = \frac{2\pi^2 \mu Z^2 e^4}{(4\pi\varepsilon_0)^2 h^2}$$

μ = reduced mass of the electron/nucleus combination:

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_{nucleus}}$$

m_e = mass of the electron

$m_{nucleus}$ = mass of the nucleus

Z = charge of the nucleus

e = electronic charge

h = Planck constant

n_h = quantum number describing the higher energy state

n_l = quantum number describing the lower energy state

$4\pi\varepsilon_0$ = permittivity of a vacuum

This equation shows that the Rydberg constant depends on the mass of the nucleus and on various fundamental constants. If the atom is hydrogen, the subscript H is commonly appended to the Rydberg constant (R_H).

Examples of the transitions observed for the hydrogen atom and the energy levels responsible are shown in **Figure 2**. As the electrons drop from level n_h to n_l, energy is released in the form of electromagnetic radiation. Conversely, if radiation of the correct energy is absorbed by an atom, electrons are raised from level n_l to level n_h. The inverse-square dependence of energy on n results in energy levels that are far apart in energy at small n and become much closer in energy at larger n. In the upper limit, as n approaches infinity, the energy approaches a limit of zero. Individual electrons can have more energy, but above this point, they are no longer part of the atom; an infinite quantum number means that the nucleus and the electron are separate entities.

EXERCISE 1

Determine the energy of the transition from $n_h = 3$ to $n_l = 2$ for the hydrogen atom, in both joules and cm^{-1} (a common unit in spectroscopy, often used as an energy unit, since $\bar{\nu}$ is proportional to E). This transition results in a red line in the visible emission spectrum of hydrogen.

When applied to the hydrogen atom, Bohr's theory worked well; however, the theory failed when atoms with two or more electrons were considered. Modifications such as elliptical rather than circular orbits were unsuccessfully introduced in attempts to fit the data to Bohr's theory.[9] The developing experimental science of atomic spectroscopy provided extensive data for testing Bohr's theory and its modifications. In spite of the efforts to "fix" the Bohr theory, the theory ultimately proved unsatisfactory; the energy levels predicted by the Bohr equation above and shown in Figure 2 are valid only for the hydrogen atom and

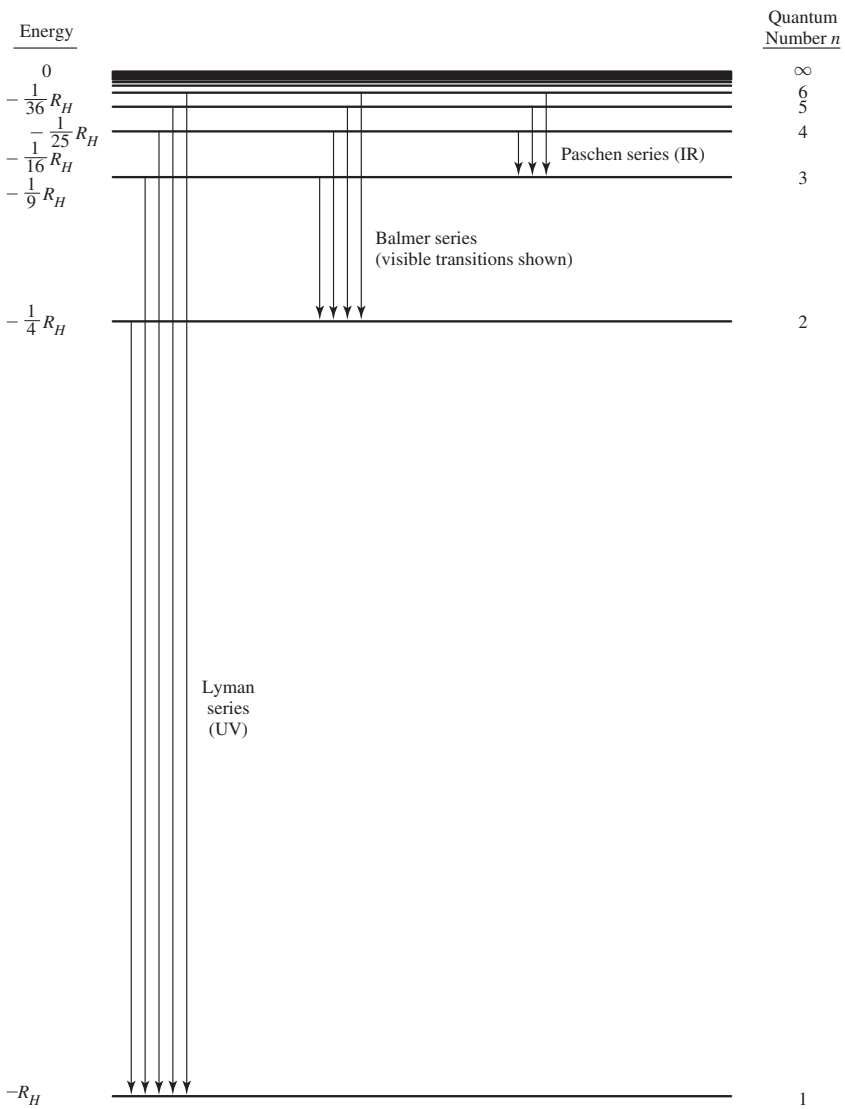


FIGURE 2 Hydrogen Atom Energy Levels.

other one-electron situations* such as He^+, Li^{2+}, and Be^{3+}. A fundamental characteristic of the electron—its wave nature—needed to be considered.

The de Broglie equation, proposed in the 1920s,[10] accounted for the electron's wave nature. According to de Broglie, all moving particles have wave properties described by the equation

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

λ = wavelength of the particle
h = Planck constant
m = mass of the particle
u = velocity of the particle

* Multiplying R_H by Z^2, the square of the nuclear charge, and adjusting the reduced mass accordingly provides an equation that describes these more exotic one-electron situations.

Particles massive enough to be visible have very short wavelengths, too small to be measured. Electrons, on the other hand, have observable wave properties because of their very small mass.

Electrons moving in circles around the nucleus, as in Bohr's theory, can be thought of as standing waves that can be described by the de Broglie equation. However, we no longer believe that it is possible to describe the motion of an electron in an atom so precisely. This is a consequence of another fundamental principle of modern physics, **Heisenberg's uncertainty principle**,[11] which states that there is a relationship between the inherent uncertainties in the location and momentum of an electron. The x component of this uncertainty is described as

$$\Delta x \, \Delta p_x \geq \frac{h}{4\pi}$$

$$\Delta x = \text{uncertainty in the position of the electron}$$

$$\Delta p_x = \text{uncertainty in the momentum of the electron}$$

The energy of spectral lines can be measured with high precision (as an example, recent emission spectral data of hydrogen atoms in the solar corona indicated a difference between $n_h = 2$ and $n_l = 1$ of 82258.9543992821(23) cm^{-1})![12] This in turn allows precise determination of the energy of electrons in atoms. This precision in energy also implies precision in momentum (Δp_x is small); therefore, according to Heisenberg, there is a large uncertainty in the location of the electron (Δx is large). This means that we cannot treat electrons as simple particles with their motion described precisely, but we must instead consider the wave properties of electrons, characterized by a degree of uncertainty in their location. In other words, instead of being able to describe precise **orbits** of electrons, as in the Bohr theory, we can only describe **orbitals**, regions that describe the probable location of electrons. The **probability** of finding the electron at a particular point in space, also called the **electron density**, can be calculated—at least in principle.

2 The Schrödinger Equation

In 1926 and 1927, Schrödinger[13] and Heisenberg[11] published papers on wave mechanics, descriptions of the wave properties of electrons in atoms, that used very different mathematical techniques. In spite of the different approaches, it was soon shown that their theories were equivalent. Schrödinger's differential equations are more commonly used to introduce the theory, and we will follow that practice.

The Schrödinger equation describes the wave properties of an electron in terms of its position, mass, total energy, and potential energy. The equation is based on the **wave function**, Ψ, which describes an electron wave in space; in other words, it describes an atomic orbital. In its simplest notation, the equation is

$$H\Psi = E\Psi$$

$$H = \text{Hamiltonian operator}$$

$$E = \text{energy of the electron}$$

$$\Psi = \text{wave function}$$

The **Hamiltonian operator**, frequently called simply the *Hamiltonian*, includes derivatives that **operate** on the wave function.* When the Hamiltonian is carried out, the result is a constant (the energy) times Ψ. The operation can be performed on any wave function

*An *operator* is an instruction or set of instructions that states what to do with the function that follows it. It may be a simple instruction such as "multiply the following function by 6," or it may be much more complicated than the Hamiltonian. The Hamiltonian operator is sometimes written $\hat{H}$ with the ^ (hat) symbol designating an operator.

describing an atomic orbital. Different orbitals have different wave functions and different values of E. This is another way of describing quantization in that each orbital, characterized by its own function Ψ, has a characteristic energy.

In the form used for calculating energy levels, the Hamiltonian operator for one-electron systems is

$$H = \underbrace{\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)}_{\text{This part of the operator describes the } \textit{kinetic energy} \text{ of the electron, its energy of motion.}} - \underbrace{\frac{Ze^2}{4\pi\varepsilon_0\sqrt{x^2 + y^2 + z^2}}}_{\text{This part of the operator describes the } \textit{potential energy} \text{ of the electron, the result of electrostatic attraction between the electron and the nucleus. It is commonly designated as } V.}$$

where

$$\begin{aligned} h &= \text{Planck constant} \\ m &= \text{mass of the electron} \\ e &= \text{charge of the electron} \\ \sqrt{x^2 + y^2 + z^2} = r &= \text{distance from the nucleus} \\ Z &= \text{charge of the nucleus} \\ 4\pi\varepsilon_0 &= \text{permittivity of a vacuum} \end{aligned}$$

This operator can be applied to a wave function Ψ,

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, z)\right]\Psi(x, y, z) = E\,\Psi(x, y, z)$$

where

$$V = \frac{-Ze^2}{4\pi\varepsilon_0 r} = \frac{-Ze^2}{4\pi\varepsilon_0\sqrt{x^2 + y^2 + z^2}}$$

The potential energy V is a result of electrostatic attraction between the electron and the nucleus. Attractive forces, such as those between a positive nucleus and a negative electron, are defined by convention to have a negative potential energy. An electron near the nucleus (small r) is strongly attracted to the nucleus and has a large negative potential energy. Electrons farther from the nucleus have potential energies that are small and negative. For an electron at infinite distance from the nucleus ($r = \infty$), the attraction between the nucleus and the electron is zero, and the potential energy is zero. The hydrogen atom energy level diagram in Figure 2 illustrates these concepts.

Because n varies from 1 to ∞, and every atomic orbital is described by a unique Ψ, there is no limit to the number of solutions of the Schrödinger equation for an atom. *Each Ψ describes the wave properties of a given electron in a particular orbital*. The probability of finding an electron at a given point in space is proportional to Ψ^2. A number of conditions are required for a physically realistic solution for Ψ:

1. The wave function Ψ must be single-valued.	There cannot be two probabilities for an electron at any position in space.
2. The wave function Ψ and its first derivatives must be continuous.	The probability must be defined at all positions in space and cannot change abruptly from one point to the next.
3. The wave function Ψ must approach zero as r approaches infinity.	For large distances from the nucleus, the probability must grow smaller and smaller (the atom must be finite).

4. The integral $\int_{all\ space} \Psi_A \Psi_A^* \, d\tau = 1$ — The total probability of an electron being *somewhere* in space $= 1$. This is called **normalizing** the wave function.*

5. The integral $\int_{all\ space} \Psi_A \Psi_B^* \, d\tau = 0$ — Ψ_A and Ψ_B are wave functions for electrons in different orbitals within the same atom. All orbitals in an atom must be orthogonal to each other. In some cases, this means that the axes of orbitals must be perpendicular, as with the p_x, p_y, and p_z orbitals.

2.1 The Particle in a Box

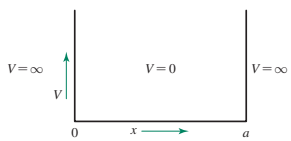


FIGURE 3 Potential Energy Well for the Particle in a Box.

A simple example of the wave equation, the particle in a one-dimensional box, shows how these conditions are used. We will give an outline of the method; details are available elsewhere.** The "box" is shown in **Figure 3**. The potential energy $V(x)$ inside the box, between $x = 0$ and $x = a$, is defined to be zero. Outside the box, the potential energy is infinite. This means that the particle is completely trapped in the box and would require an infinite amount of energy to leave the box. However, there are no forces acting on it within the box.

The wave equation for locations within the box is

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2 \Psi(x)}{\partial x^2}\right) = E\,\Psi(x), \quad \text{because } V(x) = 0$$

Sine and cosine functions have the properties we associate with waves—a well-defined wavelength and amplitude—and we may therefore propose that the wave characteristics of our particle may be described by a combination of sine and cosine functions. A general solution to describe the possible waves in the box would then be

$$\Psi = A \sin rx + B \cos sx$$

where A, B, r, and s are constants. Substitution into the wave equation allows solution for r and s (see Problem 8a at the end of the chapter):

$$r = s = \sqrt{2mE}\,\frac{2\pi}{h}$$

Because Ψ must be continuous and must equal zero at $x < 0$ and $x > a$ (because the particle is confined to the box), Ψ must go to zero at $x = 0$ and $x = a$. Because $\cos sx = 1$ for $x = 0$, Ψ can equal zero in the general solution above only if $B = 0$. This reduces the expression for Ψ to

$$\Psi = A \sin rx$$

At $x = a$, Ψ must also equal zero; therefore, $\sin ra = 0$, which is possible only if ra is an integral multiple of π:

$$ra = \pm n\pi \quad \text{or} \quad r = \frac{\pm n\pi}{a}$$

* Because the wave functions may have imaginary values (containing $\sqrt{-1}$), Ψ^* (where Ψ^* designates the complex conjugate of Ψ) is used to make the integral real. In many cases, the wave functions themselves are real, and this integral becomes $\int_{all\ space} \Psi_A^2 \, d\tau$.

** G. M. Barrow, *Physical Chemistry*, 6th ed., McGraw-Hill, New York, 1996, pp. 65, 430, calls this the "particle on a line" problem. Other physical chemistry texts also include solutions to this problem.

where n = any integer $\neq 0$.* Because both positive and negative values yield the same results, substituting the positive value for r into the solution for r gives

$$r = \frac{n\pi}{a} = \sqrt{2mE}\,\frac{2\pi}{h}$$

This expression may be solved for E:

$$E = \frac{n^2h^2}{8ma^2}$$

These are the energy levels predicted by the particle-in-a-box model for any particle in a one-dimensional box of length a. The energy levels are quantized according to **quantum numbers** $n = 1, 2, 3, \ldots$

Substituting $r = n\pi/a$ into the wave function gives

$$\Psi = A \sin \frac{n\pi x}{a}$$

And applying the normalizing requirement $\int \Psi\Psi^* d\tau = 1$ gives

$$A = \sqrt{\frac{2}{a}}$$

The total solution is then

$$\Psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

The resulting wave functions and their squares for the first three states—the ground state ($n = 1$) and first two excited states ($n = 2$ and $n = 3$)—are plotted in **Figure 4**.

The squared wave functions are the probability densities; they show one difference between classical and quantum mechanical behavior of an electron in such a box. Classical mechanics predicts that the electron has equal probability of being at any point in the box. The wave nature of the electron gives it varied probabilities at different locations in the box. The greater the square of the electron wave amplitude, the greater the probability of the electron being located at the specified coordinate when at the quantized energy defined by the Ψ.

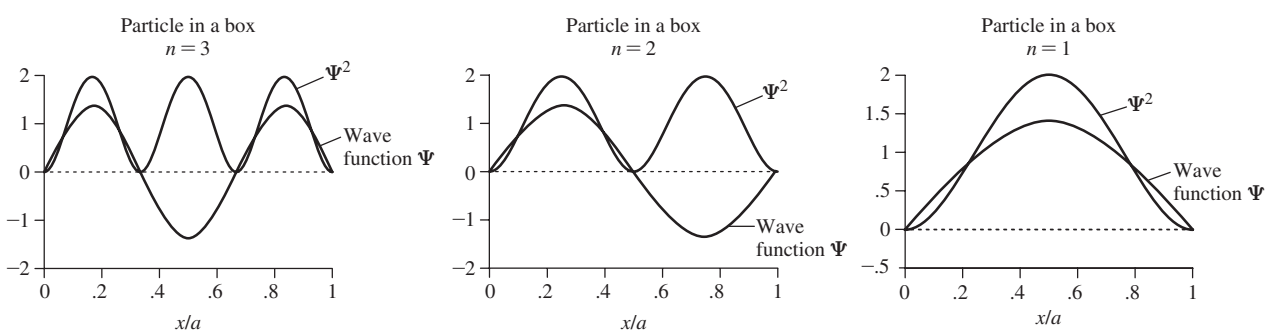


FIGURE 4 Wave Functions and Their Squares for the Particle in a Box with n = 1, 2, and 3.

* If $n = 0$, then $r = 0$ and $\Psi = 0$ at all points. The probability of finding the particle is $\int \Psi\Psi^* dx = 0$; if the particle is an electron, there is then no electron at all.

2.2 Quantum Numbers and Atomic Wave Functions

The particle-in-a-box example shows how a wave function operates in one dimension. Mathematically, atomic orbitals are discrete solutions of the three-dimensional Schrödinger equations. The same methods used for the one-dimensional box can be expanded to three dimensions for atoms. These orbital equations include three quantum numbers, n, l, and m_l. A fourth quantum number, m_s, a result of relativistic corrections to the Schrödinger equation, completes the description by accounting for the magnetic moment of the electron. The quantum numbers are summarized in **Table 2**. **Tables 3** and **4** describe wave functions.

The quantum number n is primarily responsible for determining the overall energy of an atomic orbital; the other quantum numbers have smaller effects on the energy. The quantum number l determines the angular momentum and shape of an orbital. The quantum number m_l determines the orientation of the angular momentum vector in a magnetic field, or the position of the orbital in space, as shown in Table 3. The quantum number m_s determines the orientation of the electron's magnetic moment in a magnetic field, either in the direction of the field $(+\frac{1}{2})$ or opposed to it $(-\frac{1}{2})$. When no field is present, all m_l values associated with a given n—all three p orbitals or all five d orbitals—have the same energy, and both m_s values have the same energy. Together, the quantum numbers n, l, and m_l define an atomic orbital.

The quantum number m_s describes the electron spin within the orbital. This fourth quantum number is consistent with a famous experimental observation. When a beam of alkali metal atoms (each with a single valence electron) is passed through a magnetic field, the beam splits into two parts; half the atoms are attracted by one magnet pole, and half are attracted by the opposite pole. Because in classical physics spinning charged particles generate magnetic moments, it is common to attribute an electron's magnetic moment to its spin—as if an electron were a tiny bar magnet—with the orientation of the magnetic field vector a function of the spin direction (counterclockwise vs. clockwise). However, the spin of an electron is a purely quantum mechanical property; application of classical mechanics to an electron is inaccurate.

One feature that should be mentioned is the appearance of $i(=\sqrt{-1})$ in the p and d orbital wave equations in Table 3. Because it is much more convenient to work with

TABLE 2 Quantum Numbers and Their Properties

Symbol	Name	Values	Role
n	Principal	$1, 2, 3, \ldots$	Determines the major part of the energy
l	Angular momentum*	$0, 1, 2, \ldots, n-1$	Describes angular dependence and contributes to the energy
m_l	Magnetic	$0, \pm 1, \pm 2, \ldots, \pm l$	Describes orientation in space (angular momentum in the z direction)
m_s	Spin	$\pm \frac{1}{2}$	Describes orientation of the electron spin (magnetic moment) in space

Orbitals with different l values are known by the following labels, derived from early terms for different families of spectroscopic lines:

l	0	1	2	3	4	5, …
Label	*s*	*p*	*d*	*f*	*g*	continuing alphabetically

* Also called the azimuthal quantum number.

TABLE 3 Hydrogen Atom Wave Functions: Angular Functions

Angular Factors					Real Wave Functions			
Related to Angular Momentum				Functions of θ	In Polar Coordinates	In Cartesian Coordinates	Shapes	Label
l	m_l	Φ	Θ		$\Theta\Phi(\theta, \phi)$	$\Theta\Phi(x, y, z)$		
$0(s)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$		$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{2\sqrt{\pi}}$		s
$1(p)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2}\cos\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{z}{r}$		p_z
	+1	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{x}{r}$		p_x
	−1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{3}}{2}\sin\theta$		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\frac{y}{r}$		p_y
$2(d)$	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{2}\sqrt{\frac{5}{2}}(3\cos^2\theta-1)$		$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\frac{(2z^2 - x^2 - y^2)}{r^2}$		d_{z^2}
	+1	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\cos\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{xz}{r^2}$		d_{xz}
	−1	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\frac{\sqrt{15}}{2}\cos\theta\sin\theta$		$\frac{1}{2}\sqrt{\frac{15}{\pi}}\cos\theta\sin\theta\sin\phi$	$\frac{1}{2}\sqrt{\frac{15}{\pi}}\frac{yz}{r^2}$		d_{yz}
	+2	$\frac{1}{\sqrt{2\pi}}e^{2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\cos 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{(x^2 - y^2)}{r^2}$		$d_{x^2-y^2}$
	−2	$\frac{1}{\sqrt{2\pi}}e^{-2i\phi}$	$\frac{\sqrt{15}}{4}\sin^2\theta$		$\frac{1}{4}\sqrt{\frac{15}{\pi}}\sin^2\theta\sin 2\phi$	$\frac{1}{4}\sqrt{\frac{15}{\pi}}\frac{xy}{r^2}$		d_{xy}

Source: Hydrogen Atom Wave Functions: Angular Functions, *Physical Chemistry*, 5th ed.,Gordon Barrow (c) 1988. McGraw-Hill Companies, Inc.

NOTE: The relations $(e^{i\phi} - e^{-i\phi})/(2i) = \sin\phi$ and $(e^{i\phi} + e^{-i\phi})/2 = \cos\phi$ can be used to convert the exponential imaginary functions to real trigonometric functions, combining the two orbitals with $m_l = \pm 1$ to give two orbitals with $\sin\phi$ and $\cos\phi$. In a similar fashion, the orbitals with $m_l = \pm 2$ result in real functions with $\cos^2\phi$ and $\sin^2\phi$. These functions have then been converted to Cartesian form by using the functions $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, and $z = r\cos\theta$.

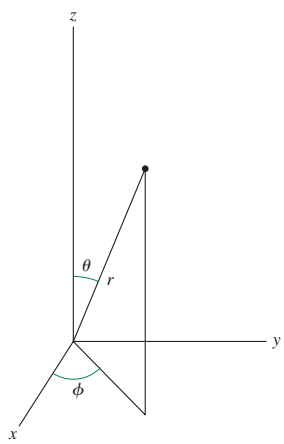
real functions than complex functions, we usually take advantage of another property of the wave equation. For differential equations of this type, any linear combination of solutions to the equation—sums or differences of the functions, with each multiplied by any coefficient—is also a solution to the equation. The combinations usually chosen for the p orbitals are the sum and difference of the p orbitals having $m_l = +1$ and –1, normalized by multiplying by the constants $\frac{1}{\sqrt{2}}$ and $\frac{i}{\sqrt{2}}$, respectively:

$$\Psi_{2p_x} = \frac{1}{\sqrt{2}}(\Psi_{+1} + \Psi_{-1}) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\left[R(r)\right]\sin\theta\cos\phi$$

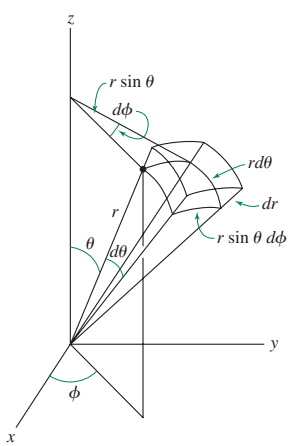
$$\Psi_{2p_y} = \frac{i}{\sqrt{2}}(\Psi_{+1} - \Psi_{-1}) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\left[R(r)\right]\sin\theta\sin\phi$$

TABLE 4 Hydrogen Atom Wave Functions: Radial Functions

Orbital	n	l	Radial Functions $R(r)$, with $\sigma = Zr/a_0$ $R(r)$
$1s$	1	0	$R_{1s} = 2\left[\frac{Z}{a_0}\right]^{3/2} e^{-\sigma}$
$2s$	2	0	$R_{2s} = 2\left[\frac{Z}{2a_0}\right]^{3/2} (2 - \sigma)e^{-\sigma/2}$
$2p$		1	$R_{2p} = \frac{1}{\sqrt{3}}\left[\frac{Z}{2a_0}\right]^{3/2} \sigma e^{-\sigma/2}$
$3s$	3	0	$R_{3s} = \frac{2}{27}\left[\frac{Z}{3a_0}\right]^{3/2} (27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$
$3p$		1	$R_{3p} = \frac{1}{81\sqrt{3}}\left[\frac{2Z}{a_0}\right]^{3/2} (6 - \sigma)\sigma\, e^{-\sigma/3}$
$3d$		2	$R_{3d} = \frac{1}{81\sqrt{15}}\left[\frac{2Z}{a_0}\right]^{3/2} \sigma^2 e^{-\sigma/3}$



Spherical coordinates



Volume element

FIGURE 5 Spherical Coordinates and Volume Element for a Spherical Shell in Spherical Coordinates.

The same procedure used on the d orbital functions for $m_l = \pm 1$ and ± 2 gives the functions in the column headed $\Theta\Phi(\theta, \phi)$ in Table 3, which are the familiar d orbitals. The d_{z^2} orbital ($m_l = 0$) actually uses the function $2z^2 - x^2 - y^2$, which we shorten to z^2 for convenience.* These functions are now real functions, so $\Psi = \Psi^*$ and $\Psi\Psi^* = \Psi^2$.

A more detailed look at the Schrödinger equation shows the mathematical origin of atomic orbitals. In three dimensions, Ψ may be expressed in terms of Cartesian coordinates (x, y, z) or in terms of spherical coordinates (r, θ, ϕ). Spherical coordinates, as shown in **Figure 5**, are especially useful in that r represents the distance from the nucleus. The spherical coordinate θ is the angle from the z axis, varying from 0 to π, and ϕ is the angle from the x axis, varying from 0 to 2π. Conversion between Cartesian and spherical coordinates is carried out with the following expressions:

$$x = r \sin\theta \cos\phi$$
$$y = r \sin\theta \sin\phi$$
$$z = r \cos\theta$$

In spherical coordinates, the three sides of the volume element are $r\,d\theta$, $r \sin\theta\, d\phi$, and dr. The product of the three sides is $r^2 \sin\theta\, d\theta\, d\phi\, dr$, equivalent to $dx\, dy\, dz$. The volume of the thin shell between r and $r + dr$ is $4\pi r^2\, dr$, which is the integral over ϕ from 0 to π and over θ from 0 to 2π. This integral is useful in describing the electron density as a function of distance from the nucleus.

Ψ can be factored into a radial component and two angular components. The **radial function *R*** describes electron density at different distances from the nucleus; the **angular functions** Θ and Φ describe the shape of the orbital and its orientation in space. The two angular factors are sometimes combined into one factor, called Y:

$$\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) = R(r)Y(\theta, \phi)$$

*We should really call this the $d_{2z^2-x^2-y^2}$ orbital!

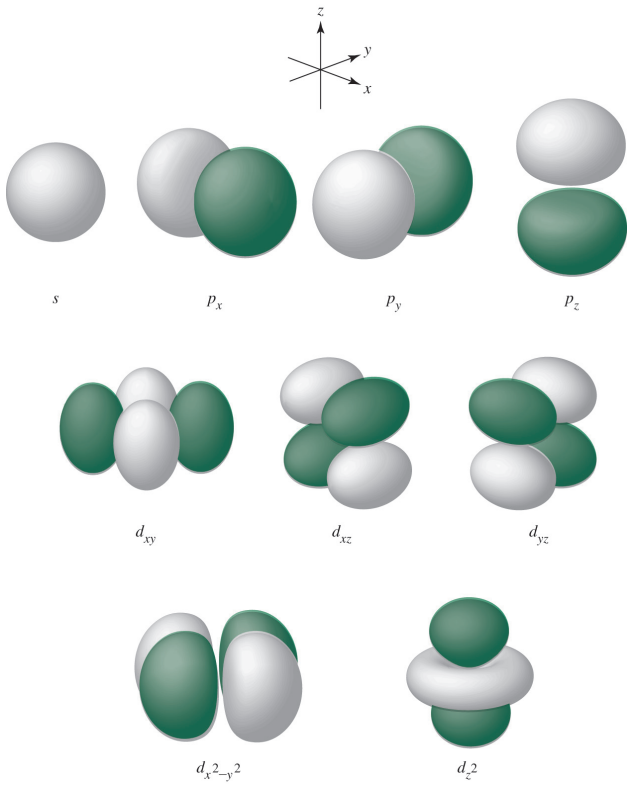


FIGURE 6 Selected Atomic Orbitals.

(Selected Atomic Orbitals by Gary O. Spessard and Gary L. Miessler. Reprinted by permission.)

R is a function only of r; Y is a function of θ and ϕ, and it gives the distinctive shapes of s, p, d, and other orbitals. R, Θ and Φ are shown separately in Tables 3 and 4.

Angular Functions

The angular functions Θ and Φ determine how the probability changes from point to point at a given distance from the center of the atom; in other words, they give the shape of the orbitals and their orientation in space. The angular functions Θ and Φ are determined by the quantum numbers l and m_l. The shapes of s, p, and d orbitals are shown in Table 3 and **Figure 6**.

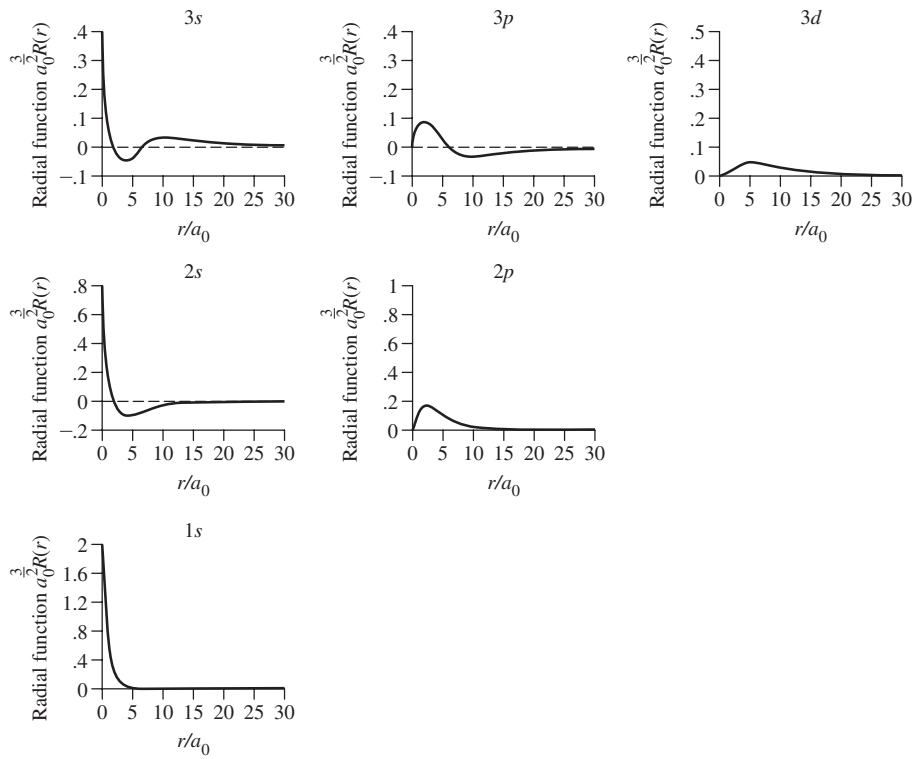
In the center of Table 3 are the shapes for the Θ portion; when the Φ portion is included, with values of $\phi = 0$ to 2π, the three-dimensional shapes in the far-right column are formed. In the three-dimensional diagrams of orbitals in Table 3, the orbital lobes are shaded where the wave function is negative. *The different shadings of the lobes represent different signs of the wave function* Ψ. It is useful to distinguish regions of opposite signs for bonding purposes.

Radial Functions

The radial factor $R(r)$ (Table 4) is determined by the quantum numbers n and l, the principal and angular momentum quantum numbers.

The **radial probability function** is $4\pi r^2R^2$. This function describes the probability of finding the electron at a given distance from the nucleus, summed over all angles, with the $4\pi r^2$ factor the result of integrating over all angles. The radial wave functions and radial probability functions are plotted for the $n = 1$, 2, and 3 orbitals in **Figure 7**. Both $R(r)$ and $4\pi r^2R^2$ are scaled with a_0, the Bohr radius, to give reasonable units on the axes of the

Radial Wave Functions



Radial Probability Functions

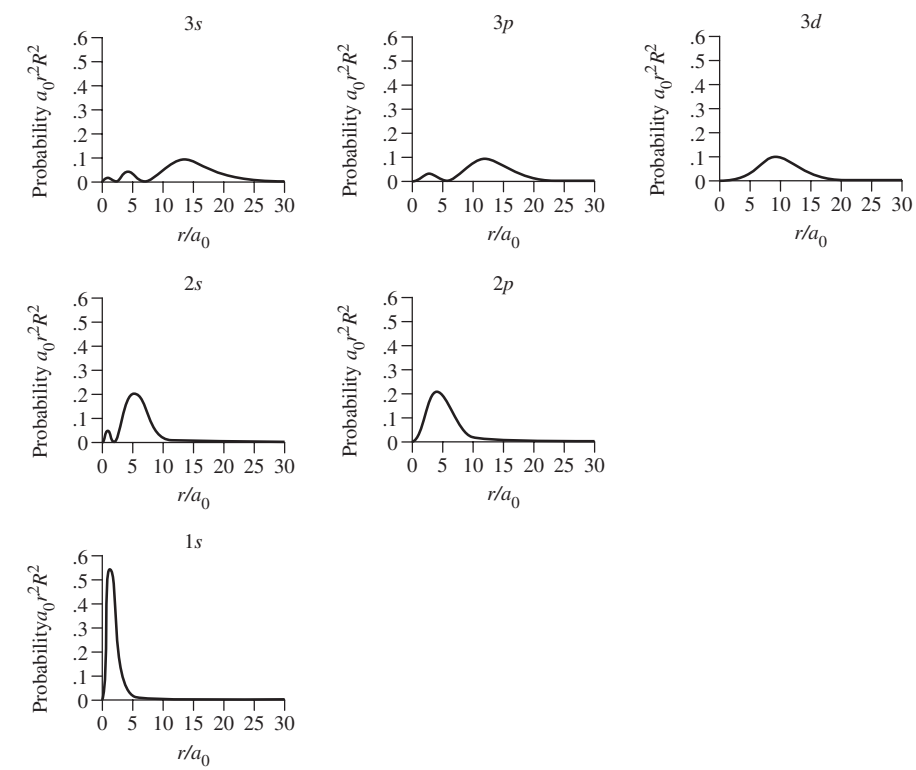


FIGURE 7 Radial Wave Functions and Radial Probability Functions.

graphs. The Bohr radius, $a_0 = 52.9$ pm, is a common unit in quantum mechanics. It is the value of r at the maximum of Ψ^2 for a hydrogen 1s orbital (the most probable distance from the hydrogen nucleus for the 1s electron), and it is also the radius of the $n = 1$ orbit according to the Bohr model.

In all the radial probability plots, the electron density, or probability of finding the electron, falls off rapidly beyond its maximum as the distance from the nucleus increases. It falls off most quickly for the 1s orbital; by $r = 5a_0$, the probability is approaching zero. By contrast, the 3d orbital has a maximum at $r = 9a_0$ and does not approach zero until approximately $r = 20a_0$. All the orbitals, including the s orbitals, have zero probability at the center of the nucleus, because $4\pi r^2R^2 = 0$ at $r = 0$. The radial probability functions are a combination of $4\pi r^2$, which increases rapidly with r, and R^2, which may have maxima and minima, but generally decreases exponentially with r. The product of these two factors gives the characteristic probabilities seen in the plots. Because chemical reactions depend on the shape and extent of orbitals at large distances from the nucleus, the radial probability functions help show which orbitals are most likely to be involved in reactions.

Nodal Surfaces

At large distances from the nucleus, the electron density, or probability of finding the electron, falls off rapidly. The 2s orbital also has a **nodal surface**, a surface with zero electron density, in this case a sphere with $r = 2a_0$ where the probability is zero. Nodes appear naturally as a result of the wave nature of the electron. A node is a surface where the wave function is zero as it changes sign (as at $r = 2a_0$ in the 2s orbital); this requires that $\Psi = 0$, and the probability of finding the electron at any point on the surface is also zero.

If the probability of finding an electron is zero ($\Psi^2 = 0$), Ψ must also be equal to zero. Because

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

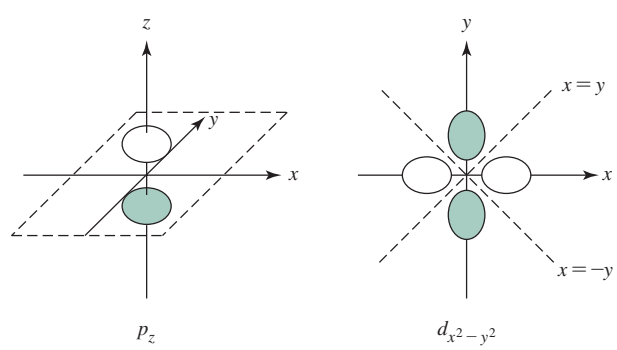
in order for $\Psi = 0$, either $R(r) = 0$ or $Y(\theta, \phi) = 0$. We can therefore determine nodal surfaces by determining under what conditions $R = 0$ or $Y = 0$.

Table 5 summarizes the nodes for several orbitals. Note that the total number of nodes in any orbital is $n - 1$ if the conical nodes of some d and f orbitals count as two nodes.*

TABLE 5 Nodal Surfaces

Angular Nodes [$Y(\theta, \phi) = 0$] Examples (number of angular nodes)	
s orbitals	0
p orbitals	1 plane for each orbital
d orbitals	2 planes for each orbital except d_{z^2}
	1 conical surface for d_{z^2}

Radial Nodes [$R(r) = 0$] Examples (number of radial nodes)					
1s	0	2p	0	3d	0
2s	1	3p	1	4d	1
3s	2	4p	2	5d	2



*Mathematically, the nodal surface for the d_{z^2} orbital is one surface, but in this instance, it fits the pattern better if thought of as two nodes.

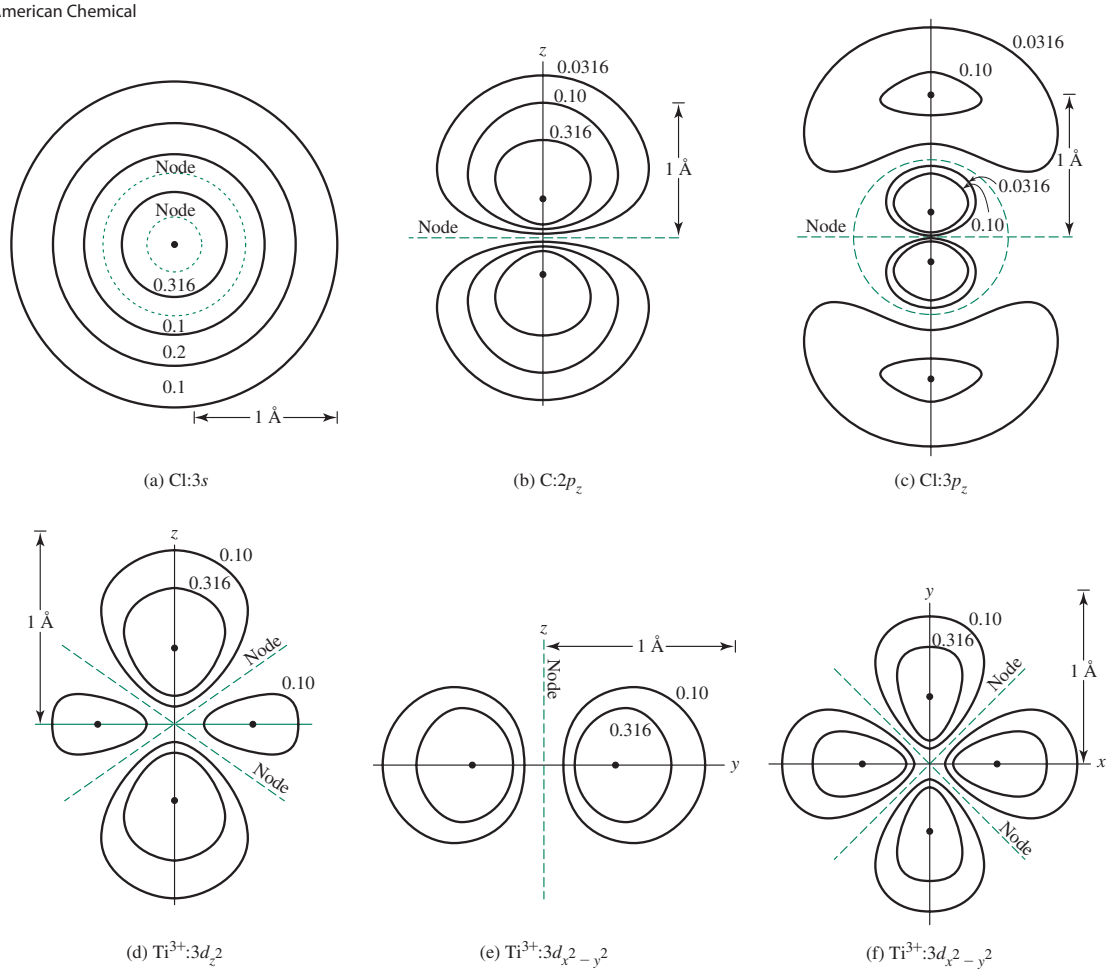
Angular nodes result when $Y = 0$, and are planar or conical. Angular nodes can be determined in terms of θ and ϕ but may be easier to visualize if Y is expressed in Cartesian (x, y, z) coordinates (see Table 3). In addition, the regions where the wave function is positive and where it is negative can be found. This information will be useful in working with molecular orbitals. There are l angular nodes in any orbital, with the conical surface in the d_{z^2} orbitals—and other orbitals having conical nodes—counted as two nodes.

Radial nodes (spherical nodes) result when $R = 0$. They give the atom a layered appearance, shown in **Figure 8** for the $3s$ and $3p_z$ orbitals. These nodes occur when the radial function changes sign; they are depicted in the radial function graphs by $R(r) = 0$ and in the radial probability graphs by $4\pi r^2R^2 = 0$. The lowest energy orbitals of each classification ($1s$, $2p$, $3d$, $4f$, etc.) have no radial nodes. The number of radial nodes increases as n increases; the number of radial nodes for a given orbital is always* equal to $n - l - 1$.

Nodal surfaces can be puzzling. For example, a p orbital has a nodal plane through the nucleus. How can an electron be on both sides of a node at the same time without ever having been at the node, at which the probability is zero? One explanation is that the probability does not go quite to zero** on the basis of relativistic arguments.

FIGURE 8 Constant Electron Density Surfaces for Selected Atomic Orbitals. (a)–(d) The cross-sectional plane is any plane containing the z axis. (e) The cross section is taken through the xz or yz plane. (f) The cross section is taken through the xy plane.

(Figures (b)–(f) Reproduced with permission from E. A. Orgyzlo and G.B. Porter, in *J. Chem. Educ.*, 40, 258. Copyright **1963**. American Chemical Society.)



(a) Cl:3s (b) C:2p_z (c) Cl:3p_z

(d) Ti^{3+}:3d_{z^2} (e) Ti^{3+}:3$d_{x^2-y^2}$ (f) Ti^{3+}:3$d_{x^2-y^2}$

* Again, counting a conical nodal surface, such as for a d_{z^2} orbital, as two nodes.

** A. Szabo, *J. Chem. Educ.*, **1969**, *46*, 678 explains that the electron probability at a nodal surface has a very small but finite value.

Another explanation is that such a question really has no meaning for an electron behaving as a wave. Recall the particle-in-a-box example. Figure 4 shows nodes at $x/a = 0.5$ for $n = 2$ and at $x/a = 0.33$ and 0.67 for $n = 3$. The same diagrams could represent the amplitudes of the motion of vibrating strings at the fundamental frequency ($n = 1$) and multiples of 2 and 3. A plucked violin string vibrates at a specific frequency, and nodes at which the amplitude of vibration is zero are a natural result. Zero amplitude does not mean that the string does not exist at these points but simply that the magnitude of the vibration is zero. An electron wave exists at the node as well as on both sides of a nodal surface, just as a violin string exists at the nodes and on both sides of points having zero amplitude.

Still another explanation, in a lighter vein, was suggested by R. M. Fuoss to one of the authors in a class on bonding. Paraphrased from St. Thomas Aquinas, "Angels are not material beings. Therefore, they can be first in one place and later in another without ever having been in between." If the word "electrons" replaces the word "angels," a semitheological interpretation of nodes would result.

EXAMPLE 1

Nodal structure of $\boldsymbol{p_z}$ The angular factor Y is given in Table 3 in terms of Cartesian coordinates:

$$Y = \frac{1}{2}\sqrt{\frac{3}{\pi}}\,\frac{z}{r}$$

This orbital is designated p_z because z appears in the Y expression. For an angular node, Y must equal zero, which is true only if $z = 0$. Therefore, $z = 0$ (the xy plane) is an angular nodal surface for the p_z orbital, as shown in Table 5 and Figure 8. The wave function is positive where $z > 0$ and negative where $z < 0$. In addition, a $2p_z$ orbital has no radial (spherical) nodes, a $3p_z$ orbital has one radial node, and so on.

Nodal structure of $\boldsymbol{d_{x^2-y^2}}$

$$Y = \frac{1}{4}\sqrt{\frac{15}{\pi}}\,\frac{(x^2 - y^2)}{r^2}$$

Here, the expression $x^2 - y^2$ appears in the equation, so the designation is $d_{x^2-y^2}$.

Because there are two solutions to the equation $Y = 0$ (setting $x^2 - y^2 = 0$, the solutions are $x = y$ and $x = -y$), the planes defined by these equations are the angular nodal surfaces. They are planes containing the z axis and making 45° angles with the x and y axes (see Table 5). The function is positive where $x > y$ and negative where $x < y$. In addition, a $3d_{x^2-y^2}$ orbital has no radial nodes, a $4d_{x^2-y^2}$ has one radial node, and so on.

EXERCISE 2 Describe the angular nodal surfaces for a d_{z^2} orbital, whose angular wave function is

$$Y = \frac{1}{4}\sqrt{\frac{5}{\pi}}\,\frac{(2z^2 - x^2 - y^2)}{r^2}$$

EXERCISE 3 Describe the angular nodal surfaces for a d_{xz} orbital, whose angular wave function is

$$Y = \frac{1}{2}\sqrt{\frac{15}{\pi}}\,\frac{xz}{r^2}$$

The result of the calculations is the set of atomic orbitals familiar to chemists. Figure 6 shows diagrams of s, p, and d orbitals, and Figure 8 shows lines of constant electron density

in several orbitals. Different shadings of the orbital lobes in Figure 6 indicate different signs of the electron wave amplitude, and the outer surfaces shown enclose 90% of the total electron density of the orbitals. The orbitals we use are the common ones used by chemists; others that are also solutions of the Schrödinger equation can be chosen for special purposes.[14]

The reader is encouraged to make use of Internet resources that display a wide range of atomic orbitals—including *f*, *g*, and higher orbitals—show radial and angular nodes, and provide additional information.*

2.3 The Aufbau Principle

Limitations on the values of the quantum numbers lead to the **aufbau** (German, *Aufbau*, *building up*) **principle**, where the buildup of electrons in atoms results from continually increasing the quantum numbers. The energy level pattern in Figure 2 describes electron behavior in a hydrogen atom, where there is only one electron. However, interactions between electrons in polyelectronic atoms require that the order of filling orbitals be specified when more than one electron is in the same atom. In this process, we start with the lowest n, l, and m_l values (1, 0, and 0, respectively) and either of the m_s values (we will arbitrarily use $+\frac{1}{2}$ first). Three rules will then give us the proper order for the remaining electrons, as we increase the quantum numbers in the order m_l, m_s, l, and n.

1. Electrons are placed in orbitals to give the lowest total electronic energy to the atom. This means that the lowest values of n and l are filled first. Because the orbitals within each subshell (p, d, etc.) have the same energy, the orders for values of m_l and m_s are indeterminate.
2. The **Pauli exclusion principle**[15] requires that each electron in an atom have a unique set of quantum numbers. At least one quantum number must be different from those of every other electron. This principle does not come from the Schrödinger equation, but from experimental determination of electronic structures.
3. **Hund's rule of maximum multiplicity**[16] requires that electrons be placed in orbitals to give the maximum total spin possible (the maximum number of parallel spins). Two electrons in the same orbital have a higher energy than two electrons in different orbitals because of electrostatic repulsion (see below); electrons in the same orbital repel each other more than electrons in separate orbitals. Therefore, this rule is a consequence of the lowest possible energy rule (Rule 1). When there are one to six electrons in a p subshell, the required arrangements are those given in **Table 6**. (The **spin multiplicity** is the number of unpaired electrons plus 1, or $n + 1$). Any other arrangement of electrons results in fewer unpaired electrons.**

TABLE 6 Hund's Rule and Multiplicity

Number of Electrons	Arrangement	Unpaired e^-	Multiplicity
1	↑ ___ ___	1	2
2	↑ ___ ↑ ___ ___	2	3
3	↑ ___ ↑ ___ ↑ ___	3	4
4	↑↓ ___ ↑ ___ ↑ ___	2	3
5	↑↓ ___ ↑↓ ___ ↑ ___	1	2
6	↑↓ ___ ↑↓ ___ ↑↓ ___	0	1

* Two examples are http://www.orbitals.com and http://winter.group.shef.ac.uk/orbitron.
** This is only one of Hund's rules.

Hund's rule is a consequence of the energy required for pairing electrons in the same orbital. When two negatively charged electrons occupy the same region of space (same orbital) in an atom, they repel each other, with a **Coulombic energy of repulsion**, Π_c, per pair of electrons. As a result, this repulsive force favors electrons in different orbitals (different regions of space) over electrons in the same orbitals.

In addition, there is an **exchange energy**, Π_e, which arises from purely quantum mechanical considerations. This energy depends on the number of possible exchanges between two electrons with the same energy and the same spin. For example, the electron configuration of a carbon atom is $1s^2\,2s^2\,2p^2$. The $2p$ electrons can be placed in the p orbitals in three ways:

(1) ↑ ↓ ___ ___ (2) ↑ ___ ↓ ___ ___ (3) ↑ ___ ↑ ___ ___

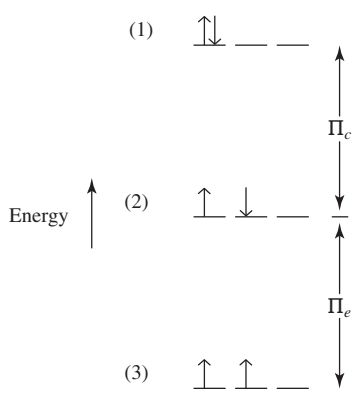
Each of these corresponds to a state having a particular energy. State (1) involves Coulombic energy of repulsion, Π_c, because it is the only one that pairs electrons in the same orbital. The energy of this state is higher than that of the other two by Π_c as a result of electron–electron repulsion.

In the first two states, there is only one possible way to arrange the electrons to give the same diagram, because there is only a single electron in each having + or – spin; these electrons can be distinguished from each other on this basis. However, in the third state, the electrons have the same spin and are therefore indistinguishable from each other. Therefore, there are two possible ways in which the electrons can be arranged:

↑ 1 ___ ↑ 2 ___ ___ ↑ 2 ___ ↑ 1 ___ ___ (one exchange of electrons)

Because there are two possible ways in which the electrons in state (3) can be arranged, we can say that there is *one pair* of possible exchanges between these arrangements, described as *one exchange of parallel electrons*. The energy involved in such an exchange of parallel electrons is designated Π_e; each exchange stabilizes (lowers the energy of) an electronic state, favoring states with more parallel spins (Hund's rule). Therefore, state (3), which is stabilized by one exchange of parallel electrons, is lower in energy than state (2) by Π_e.

The results of considering the effects of Coulombic and exchange energies for the p^2 configuration may be summarized in an energy diagram:



State (3) is the most stable; its electrons are in separate orbitals and have parallel spin; because state (3) has one possible exchange of electrons with parallel spin, it is lower in energy than state (2) by Π_e. State (1) is highest in energy because it has two electrons in the same orbital and is therefore higher in energy than state (2) by Π_c. Neither state (1) nor state (2) is stabilized by exchange interactions (zero Π_e).

In summary:

Coulombic energy of repulsion Π_c is a consequence of repulsion between electrons in the same orbital; the greater the number of such paired electrons, the higher the energy of the state.*

Exchange energy Π_e is a consequence of parallel electron spins in separate orbitals; the greater the number of such parallel spins (and consequently the greater the number of exchanges), the lower the energy of the state.

Both Coulombic and exchange energies must be taken into account when comparing the energies of different electronic states.

EXAMPLE 2

Oxygen

With four *p* electrons, oxygen could have two unpaired electrons (↑↓ ↑ ↑), or it could have no unpaired electrons (↑↓ ↑↓ ___).

a. Determine the number of electrons that could be exchanged in each case, and find the Coulombic and exchange energies.

↑↓ ↑ ↑ This configuration has one pair, energy contribution Π_c.

↑↓ ↑ ↑ One electron with ↓ spin and no possibility of exchange.

↑↓ ↑ ↑ Four possible arrangements for electrons with ↑ spin; three exchange possibilities (1–2, 1–3, 2–3), shown below; energy contribution $3\Pi_e$.

↑1 ↑2 ↑3 ↑2 ↑1 ↑3 ↑3 ↑2 ↑1 ↑1 ↑3 ↑2

Overall, $3\Pi_e + \Pi_c$.

↑↓ ↑↓ ___ has two pairs in the same orbitals and one exchange possibility for each spin pair.

Overall, $2\Pi_e + 2\Pi_c$.

b. Which state, ↑↓ ↑ ↑, or ↑↓ ↑↓ ___, is lower in energy?

The state ↑↓ ↑ ↑ is lower in energy because it has less Coulombic energy of repulsion (Π_c in comparison with $2\Pi_c$) and is stabilized by a greater number of exchanges ($3\Pi_e$ in comparison with $2\Pi_e$).

EXERCISE 4 A third possible state for the p^4 configuration would be ↑↓ ↑ ↓. Determine the Coulombic and exchange energies of this state, and compare its energy with the energies of the states determined in the preceding example. Draw a sketch showing the relative energies of these three states for oxygen's p^4 configuration.

EXERCISE 5 A nitrogen atom, with three 2*p* electrons, could have three unpaired electrons (↑ ↑ ↑), or it could have one unpaired electron (↑↓ ↑ ___).

a. Determine the number of electrons that could be exchanged in each case and the Coulombic and exchange energies. Which state would be lower in energy?

*In atoms with more than one electron (polyelectronic atoms), all electrons are subject to some Coulombic repulsion energy, but this contribution is significantly higher for electrons that are paired within atomic orbitals.

b. A third possible state for a $2p^3$ configuration would be $\underline{\uparrow}\ \underline{\uparrow}\ \underline{\downarrow}$. Determine its Coulombic and exchange energies, and compare the energy of this state with the energies determined in part **a.**

When the orbitals are **degenerate** (have the same energy), both Coulombic and exchange energies favor unpaired configurations over paired configurations. However, if there is a difference in energy between the levels involved, this difference, together with the Coulombic and exchange energies, determines the final configuration, with the configuration of lowest energy expected as the ground state; energy minimization is the driving force. For atoms, this usually means that one subshell (s, p, d) is filled before another has any electrons. However, this approach is insufficient in some transition elements, because the $4s$ and $3d$ (or the higher corresponding levels) are so close in energy that the sum of the Coulombic and exchange terms is nearly the same as the difference in energy between the $4s$ and $3d$. Section 2.4 considers these cases.

Many schemes have been used to predict the order of filling of atomic orbitals. Klechkowsky's rule states that the order of filling of the orbitals proceeds from the lowest available value for the sum $n + l$. When two combinations have the same value, the one with the smaller value of n is filled first; thus, $4s(n + l = 4 + 0)$ fills before $3d(n + l = 3 + 2)$. Combined with the other rules, this gives the order of filling of most of the orbitals.*

One of the simplest methods that fits most atoms uses the periodic table organized as in **Figure 9**. The electron configurations of hydrogen and helium are clearly $1s^1$ and $1s^2$. After that, the elements in the first two columns on the left (Groups 1 and 2) are filling s orbitals, with $l = 0$; those in the six columns on the right (Groups 13 to 18) are filling p orbitals, with $l = 1$; and the ten in the middle (the transition elements, Groups 3 to 12) are filling

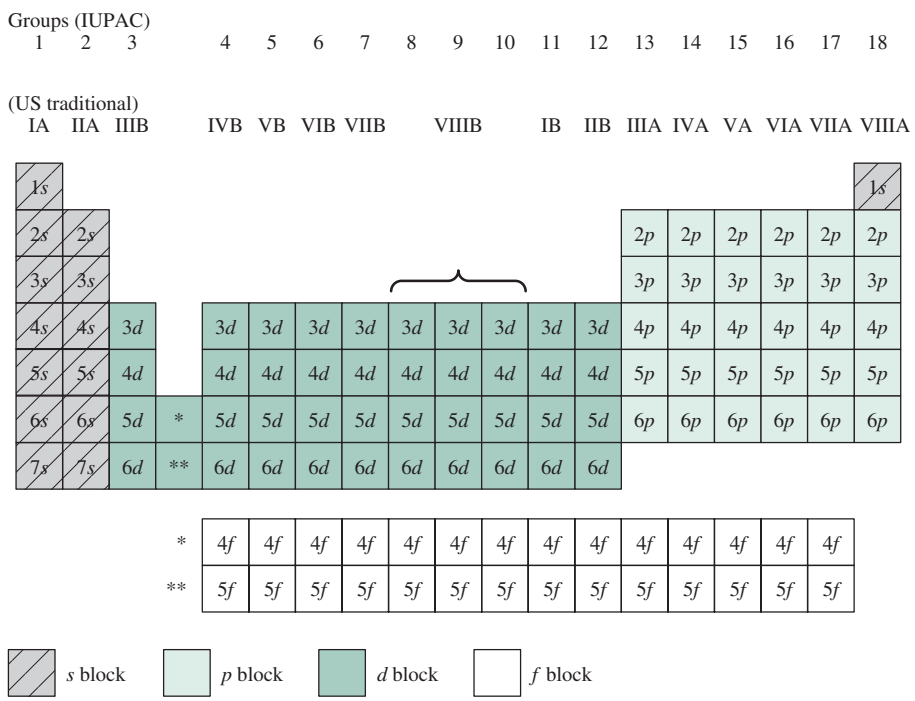


FIGURE 9 Atomic Orbital Filling in the Periodic Table.

* For recent perspective on electron configurations, energies of atomic orbitals, the periodic system, and related topics, see S-G. Wang and W. H. E. Schwarz, *Angew. Chem. Int. Ed.*, **2009**, *48*, 3404.

d orbitals, with $l = 2$. The lanthanide and actinide series (numbers 58 to 71 and 90 to 103) are filling *f* orbitals, with $l = 3$. These two methods are oversimplifications, as shown in the following paragraphs, but they do fit most atoms and provide starting points for the others.

2.4 Shielding

In polyelectronic atoms, energies of specific levels are difficult to predict quantitatively. A useful approach to such predictions uses the concept of shielding: each electron acts as a shield for electrons farther from the nucleus, reducing the attraction between the nucleus and the more distant electrons.

Although the quantum number *n* is most important in determining the energy, quantum number *l* must also be included in calculating the energy in atoms having more than one electron. As the atomic number increases, electrons are drawn toward the nucleus, and the orbital energies become more negative. Although the energies decrease with increasing *Z*, the changes are somewhat irregular because of the shielding of outer electrons by inner electrons. The electron configurations of atoms from the resulting order of orbital filling are shown in **Table 7**.

As a result of shielding and other subtle interactions between electrons, exclusive reliance on *n* to rank orbital energies (higher energy with higher quantum number *n*), which works for one-electron species, holds only for orbitals with lowest values of *n* (see **Figure 10**) in polyelectronic species. In multielectron atoms (and ions), for higher values of *n*, as the split in orbital energies with different values of quantum number *l* becomes comparable in magnitude to the differences in energy caused by *n*, the simplest order does not hold.

> For example, consider the $n = 3$ and $n = 4$ sets in Figure 10. For many atoms the 4*s* orbital is lower in energy than the 3*d* orbitals; consequently the order of filling is …3*s*, 3*p*, 4*s*, 3*d*, 4*p*… rather than the order based strictly on increasing *n* …3*s*, 3*p*, 3*d*, 4*s*, 4*p*…
>
> Similarly, 5*s* begins to fill before 4*d*, and 6*s* before 5*d*. Other examples can be found in Figure 10.

Slater[17] formulated rules that serve as an approximate guide to this effect. These rules define the effective nuclear charge Z^* as a measure of the attraction of the nucleus for a particular electron:

$$\text{Effective nuclear charge } Z^* = Z - S, \text{ where } Z = \text{nuclear charge}, \quad S = \text{shielding constant}$$

Slater's rules for determining *S* for a specific electron:*

1. The atom's electronic structure is written in order of increasing quantum numbers *n* and *l*, grouped as follows:

   (1*s*) (2*s*, 2*p*) (3*s*, 3*p*) (3*d*) (4*s*, 4*p*) (4*d*) (4*f*) (5*s*, 5*p*) (5*d*) (and so on)

2. Electrons in groups to the right in this list do not shield electrons to their left.
3. The shielding constant *S* for electrons in these groups can now be determined. For *ns* and *np* valence electrons:
   a. Each electron in the same group contributes 0.35 to the value of *S* for each other electron in the group.
   Exception: A 1*s* electron contributes 0.30 to *S* for another 1*s* electron.
   Example: For a configuration $2s^2\,2p^5$, a particular 2*p* electron has six other electrons in the (2*s*, 2*p*) group. Each of these contributes 0.35 to the value of *S*, for a total contribution to *S* of $6 \times 0.35 = 2.10$.

* Slater's original numbering scheme has been changed for convenience.

TABLE 7 Electron Configurations of the Elements

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

* Elements with configurations that do not follow the simple order of orbital filling.

[a] Evidence for elements 113–118 has been reviewed by IUPAC; see R. C. Barber, P. J. Karol, H. Nakahara, E. Vardaci, E. W. Vogt, *Pure Appl. Chem.*, **2011**, *83*, 1485. In May 2012, IUPAC officially named element 114 (flerovium, symbol Fl) and element 116 (livermorium, Lv).

Source: Actinide configurations are from J. J. Katz, G. T. Seaborg, and L. R. Morss, *The Chemistry of the Actinide Elements*, 2nd ed., Chapman and Hall, New York and London, 1986. Configurations for elements 100 to 112 are predicted, not experimental.

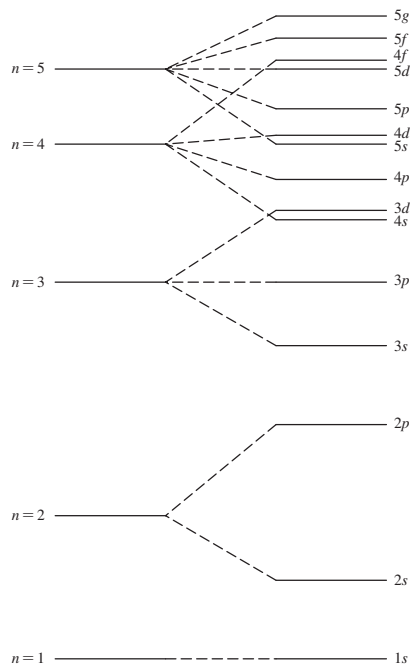


FIGURE 10 Energy Level Splitting and Overlap. The differences between the upper levels are exaggerated for easier visualization. This diagram provides unambiguous electron configurations for elements hydrogen to vanadium.

b. Each electron in $n - 1$ groups contribute 0.85 to S.
Example: For the 3s electron of sodium, there are eight electrons in the (2s, 2p) group. Each of these electrons contributes 0.85 to the value of S, a total contribution of $8 \times 0.85 = 6.80$.

c. Each electron in $n - 2$ or lower groups contributes 1.00 to S.

4. For *nd* and *nf* valence electrons:

a. Each electron in the same group contributes 0.35 to the value of S for each other electron in the group. (Same rule as **3a.**)

b. Each electron in groups to the left contributes 1.00 to S.

These rules are used to calculate the shielding constant S for valence electrons. Subtracting S from the total nuclear charge Z gives the effective nuclear charge Z^* on the selected electron:

$$Z^* = Z - S$$

Calculations of S and Z^* follow.

EXAMPLE 3

Oxygen

Use Slater's rules to calculate the shielding constant and effective nuclear charge of a 2p electron.

Rule 1: The electron configuration is written using Slater's groupings, in order:

$$(1s^2)(2s^2, 2p^4)$$

To calculate S for a valence 2p electron:

Rule 3a: Each other electron in the ($2s^2$, $2p^4$) group contributes 0.35 to S.
Total contribution $= 5 \times 0.35 = 1.75$

Rule 3b: Each 1s electron contributes 0.85 to S.
Total contribution $= 2 \times 0.85 = 1.70$

Total $S = 1.75 + 1.70 = 3.45$
Effective nuclear charge $Z^* = 8 - 3.45 = 4.55$
So rather than feeling the full +8 nuclear charge, a $2p$ electron is calculated to feel a charge of +4.55, or about 57% of the full nuclear charge.

Nickel

Use Slater's rules to calculate the shielding constant and effective nuclear charge of a $3d$ and $4s$ electron.

Rule 1: The electron configuration is written $(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^8)(4s^2)$

For a $3d$ electron:

Rule 4a: Each other electron in the $(3d^8)$ group contributes 0.35 to S.
Total contribution $= 7 \times 0.35 = 2.45$

Rule 4b: Each electron in groups to the left of $(3d^8)$ contributes 1.00 to S.
Total contribution $= 18 \times 1.00 = 18.00$
Total $S = 2.45 + 18.00 = 20.45$
Effective nuclear charge $Z^* = 28 - 20.45 = 7.55$

For a $4s$ electron:

Rule 3a: The other electron in the $(4s^2)$ group contributes 0.35 to S.

Rule 3b: Each electron in the $(3s^2, 3p^6)(3d^8)$ groups $(n - 1)$ contributes 0.85.
Total contribution $= 16 \times 0.85 = 13.60$

Rule 3c: Each other electron to the left contributes 1.00. Total contribution $=$ $10 \times 1.00 = 10.00$

Total $S = 0.35 + 13.60 + 10.00 = 23.95$

Effective nuclear charge $Z^* = 28 - 23.95 = 4.05$

The effective nuclear charge for the $4s$ electron is considerably smaller than the value for the $3d$ electron. This is equivalent to stating that the $4s$ electron is held less tightly than the $3d$ and should therefore be the first removed in ionization. This is consistent with experimental observations on nickel compounds. Ni^{2+}, the most common oxidation state of nickel, has a configuration of [Ar] $3d^8$, rather than [Ar] $3d^6 4s^2$, corresponding to loss of the $4s$ electrons from nickel atoms. All the transition metal atoms follow this same pattern of losing ns electrons more readily than $(n - 1)d$ electrons.

EXERCISE 6 Calculate the effective nuclear charge on a $5s$, $5p$, and $4d$ electron in a tin atom.

EXERCISE 7 Calculate the effective nuclear charge on a $7s$, $5f$, and $6d$ electron in a uranium atom.

Justification for Slater's rules comes from the electron probability curves for the orbitals; Slater devised these rules semiempirically using equations modeled after wavefunction equations to fit experimental data for atoms. Slater's approach results in rules that provide useful approximations for the effective nuclear charge an electron in an atom actually experiences after shielding is taken into account. The s and p orbitals have higher probabilities near the nucleus than do d orbitals of the same n, as shown earlier in Figure 7. Therefore, the shielding of $3d$ electrons by $(3s, 3p)$ electrons is calculated as 100% effective, a contribution of 1.00. At the same time, shielding of $3s$ or $3p$ electrons by $(2s, 2p)$ electrons is estimated as 85% effective, a contribution of 0.85, because the $3s$ and $3p$ orbitals have regions of significant probability close to the nucleus. Therefore, electrons in these orbitals are not completely shielded by $(2s, 2p)$ electrons.

A complication arises at Cr ($Z = 24$) and Cu ($Z = 29$) in the first transition series and in an increasing number of atoms with higher atomic numbers in the second and third transition series. This effect places an extra electron in the $3d$ level and removes one electron from the $4s$ level. Cr, for example, has a configuration of [Ar] $4s^1\ 3d^5$ rather than [Ar] $4s^2\ 3d^4$. Traditionally, this phenomenon has often been explained as a consequence of the "special stability of half-filled subshells." Half-filled and filled d and f subshells are, in fact, fairly common, as shown in **Figure 11**. A more complete explanation considers both the effects of increasing nuclear charge on the energies of the $4s$ and $3d$ levels and the interactions between electrons sharing the same orbital.[18] This approach requires totaling all contributions to the energy of the configuration of electrons, including the Coulombic and exchange energies; results of the complete calculations are consistent with the configurations determined by experimental data.

Slater's rules have been refined to improve their match with experimental data. One relatively simple refinement is based on the ionization energies for the elements hydrogen through xenon, and it provides a calculation procedure similar to that proposed by Slater.[19] A more elaborate method incorporates exponential screening and provides energies that are in closer agreement with experimental values.[20]

Another explanation that is more pictorial and considers electron–electron interactions was proposed by Rich.[21] He explained electronic structures of atoms by considering the difference in energy between the energy of one electron in an orbital and two electrons in the same orbital. Although the orbital itself is usually assumed to have only one energy, the electrostatic repulsion of the two electrons in one orbital adds the electron-pairing energy described in Section 2.3 as part of Hund's rule. We can visualize two parallel energy levels, each with electrons of only one spin, separated by the electron-pairing energy, as shown in **Figure 12**.

For example, an Sc atom has the valence configuration $4s^2\ 3d^1$. By Rich's approach, the first electron is arbitrarily considered to have $m_s = -\frac{1}{2}$. The second electron, with $m_s = +\frac{1}{2}$, completes the $4s^2$ configuration—but the total energy of these two electrons is greater than twice the energy of the first electron, because of the Coulombic energy of repulsion, Π_c. In Figure 12(a) Sc is shown as having three electrons: in ascending order these are $4s$ ($m_s = -\frac{1}{2}$), $4s$ ($m_s = +\frac{1}{2}$), and $3d$ ($m_s = -\frac{1}{2}$). The next element, Ti, also

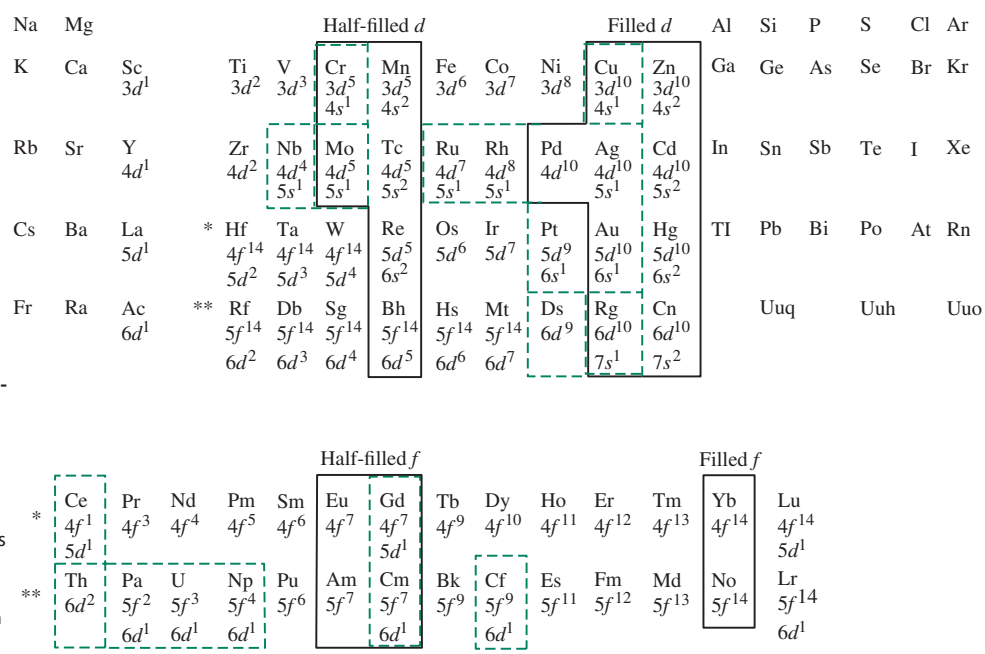


FIGURE 11 Electron Configurations of Transition Metals, Including Lanthanides and Actinides. Solid lines surrounding elements designate filled (d^{10} or f^{14}) or half-filled (d^5 or f^7) subshells. Dashed lines surrounding elements designate irregularities in sequential orbital filling, also found within some of the solid lines.

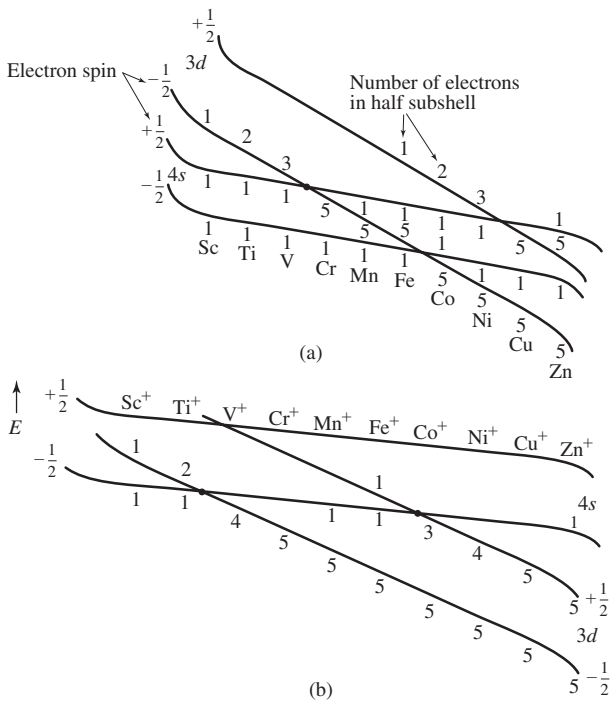


FIGURE 12 Schematic Energy Levels for Transition Elements. (a) Schematic interpretation of electron configurations for transition elements in terms of intraorbital repulsion and trends in subshell energies. (b) A similar diagram for ions, showing the shift in the crossover points on removal of an electron. The shift is even more pronounced for metal ions having 2+ or greater charges. As a consequence, transition-metal ions with 2+ or greater charges have no *s* electrons, only *d* electrons in their outer levels. Similar diagrams, although more complex, can be drawn for the heavier transition elements and the lanthanides.

(Rich, R. L., *Periodic Coorelate*, 1st Ed., (c) 1965. Reprinted and Electronically reproduced by permission of Pearson Education Inc, Upper Saddle River, NJ 07458.)

has one 4*s* electron with each spin, then two 3*d* electrons, each with $m_s = -\frac{1}{2}$. The two 3*d* electrons, by Hund's rule, have parallel spin.

As the number of protons in the nucleus increases, the effective nuclear charge for all electrons increases and the energy levels decrease in energy; their electrons become more stable. Figure 12 illustrates that the energy of the 3*d* subshell decreases more dramatically relative to 4*s* as one moves across the first transition series; this trend generally holds for $(n - 1)d$ and *ns* orbitals. A rationalization for this trend is that orbitals with shorter most probable distances to the nucleus are stabilized more as *Z* increases relative to orbitals with greater most probable distances. Because the 3*d* orbitals have shorter most probable distances from the nucleus than the 4*s* orbital, the 3*d* orbitals are stabilized more than the 4*s* as the nuclear charge increases.

The effective nuclear charge that an electron experiences generally increases as the most probable distance of the electron from the nucleus decreases; these electrons are less susceptible to shielding by electrons farther from the nucleus (for example, in Slater's rules electrons with greater most probable distances to the electron in question do not contribute at all to *S*). Since the most probable distance from the nucleus increases as *n* increases (Figure 7), the 3*d* subshell ultimately stabilizes its electrons more than the 4*s* orbital once *Z* gets sufficiently high. Regardless of the relative orbital energies, the observed electronic configuration is always the one of lowest energy. Electrons fill the lowest available orbitals in order up to their capacity, with the results shown in Figure 12 and in Table 7.

The schematic diagram in Figure 12(a) shows the order in which the levels fill, from bottom to top in energy. For example, Ti has two 4*s* electrons, one in each spin level, and two 3*d* electrons, both with the same spin. Fe has two 4*s* electrons, one in each spin level, five 3*d* electrons with spin $-\frac{1}{2}$, and one 3*d* electron with spin $+\frac{1}{2}$. For vanadium, the first two electrons enter the 4*s*, $-\frac{1}{2}$ and 4*s*, $+\frac{1}{2}$ levels; the next three are all in the 3*d*, $-\frac{1}{2}$ level, and vanadium has the configuration $4s^2\ 3d^3$. The 3*d*, $-\frac{1}{2}$ line crosses the 4*s*, $+\frac{1}{2}$ line between V and Cr. When the six electrons of chromium are filled in from the lowest level,

chromium has the configuration $4s^1\ 3d^5$. A similar crossing gives copper its $4s^1\ 3d^{10}$ structure. This approach to electron configurations of transition metals does not depend on the stability of half-filled shells or other additional factors.

Formation of a positive ion by removal of an electron reduces shielding; the effective nuclear charge for all electrons increases dramatically. On the basis of the most probable distance effect discussed previously, $(n - 1)d$ orbitals will be lower in energy than ns orbitals in the cation, as shown in Figure 12(b). As a result, the remaining electrons occupy the d orbitals. A common rule in introductory chemistry is that electrons with highest n—in this case, those in the s orbitals—are always removed first when ions are formed from the transition elements. A perhaps more mature perspective on this idea is that regardless of which electron is lost to form a transition metal ion, the lowest energy electron configuration of the resulting ion will always exhibit the vacancy in the ns orbital. This effect is even stronger for 2+ ions, where the effective nuclear charge is even higher. *Transition metal cations have no s electrons, only d electrons in their outer levels.*

A similar, but more complex, crossing of levels appears in the lanthanide and actinide series. The simple explanation would have these elements start filling f orbitals at lanthanum (57) and actinium (89), but these atoms have one d electron instead. Other elements in these series also show deviations from the "normal" sequence. Rich has explained these situations using similar diagrams.[21]

3 Periodic Properties of Atoms

A valuable aspect of the arrangment of atoms on the basis of similar electronic configurations within the periodic table is that an atom's position provides information about its properties. Some of these properties, and how they vary across periods and groups, are now discussed.

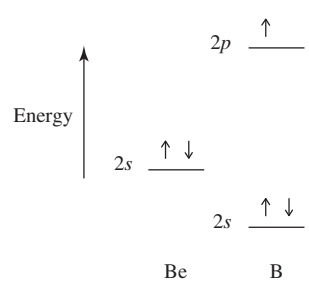
3.1 Ionization Energy

The ionization energy, also known as the *ionization potential*, is the energy required to remove an electron from a gaseous atom or ion:

$$A^{n+}(g) \longrightarrow A^{(n+1)+}(g) + e^- \qquad \text{ionization energy } (IE) = \Delta U$$

where $n = 0$ (first ionization energy), $n = 1$ (second ionization energy), and so on.

As would be expected from the effects of shielding, the ionization energy varies with different nuclei and different numbers of electrons. Trends for the first ionization energies of the early elements in the periodic table are shown in **Figure 13**. The general trend across a period is an increase in ionization energy as the nuclear charge increases. However, the experimental values show a break in the trend in the second period at boron and again at oxygen. Because boron is the first atom to have an electron in a higher energy $2p$ orbital that is shielded somewhat by the $2s$ electrons, boron's $2p$ electron is more easily lost than the $2s$ electrons of beryllium; boron has the lower ionization energy.



At the fourth $2p$ electron, at oxygen, a similar decrease in ionization energy occurs. Here, the fourth electron shares an orbital with one of the three previous $2p$ electrons

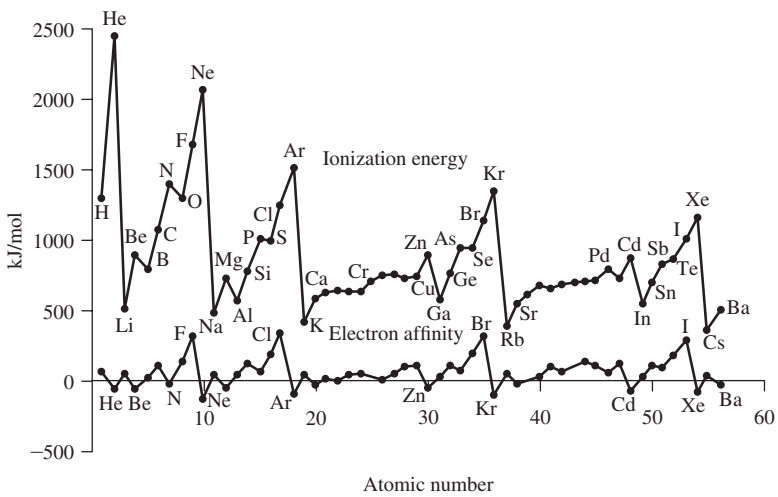


FIGURE 13 Ionization Energies and Electron Affinities. Ionization energy $= \Delta U$ for $M(g) \longrightarrow M^+(g) + e^-$

(Data from C. E. Moore, *Ionization Potentials and Ionization Limits, National Standards Reference Data Series*, U.S. National Bureau of Standards, Washington, DC, **1970**, NSRDS-NBS 34) Electron affinity $= \Delta U$ for $M^-(g) \longrightarrow M(g) + e^-$ Data from H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, **1985,** *14*, 731). Numerical values are in Appendices B-2 and B-3.

(↑↓ ↑ ↑), and the repulsion between the paired electrons (Π_c) reduces the energy necessary to remove an electron from oxygen; oxygen has a lower ionization energy than nitrogen, which has the $2p$ configuration ↑ ↑ ↑.

Similar patterns appear in the other periods, for example Na through Ar and K through Kr, omitting the transition metals. The transition metals have less dramatic differences in ionization energies, with the effects of shielding and increasing nuclear charge more nearly in balance.

Much larger decreases in ionization energy occur at the start of each new period, because the change to the next major quantum number requires that the new *s* electron have a much higher energy. The maxima at the noble gases decrease with increasing *Z*, because the outer electrons are farther from the nucleus in the heavier elements. Overall, the trends are toward higher ionization energy from left to right in the periodic table (the major change) and lower ionization energy from top to bottom (a minor change). The differences described in the previous paragraph are superimposed on these more general changes.

3.2 Electron Affinity

Electron affinity can be defined as the energy required to remove an electron from a negative ion:*

$$A^-(g) \longrightarrow A(g) + e^- \qquad \text{electron affinity } (EA) = \Delta U$$

Because of the similarity of this reaction to the ionization for an atom, electron affinity is sometimes described as the *zeroth ionization energy*. This reaction is endothermic (positive ΔU) except for the noble gases and the alkaline earth elements. The pattern of electron affinities with changing *Z,* shown in Figure 13, is similar to that of the ionization energies, but for one larger *Z* value (one more electron for each species) and with much smaller absolute numbers. For either of the reactions, removal of the first electron past a noble gas configuration is easy, so the noble gases have the lowest electron affinities. The electron affinities are all much smaller than the corresponding ionization energies, because electron removal from a negative ion (that features more shielding of the nuclear charge) is easier than removal from a neutral atom.

Comparison of the ionization and electron affinity graphs in Figure 13 shows similar zigzag patterns, but with the two graphs displaced by one element: for example, electron affinity shows a peak at F and valley at Ne, and ionization energy a peak at Ne and valley at

*Historically, the definition has been $-\Delta U$ for the reverse reaction, adding an electron to the neutral atom. The definition we use avoids the sign change.

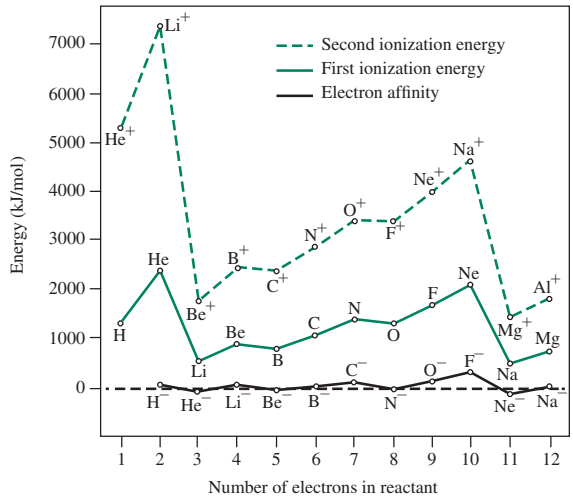


FIGURE 14 First and Second Ionization Energies and Electron Affinities

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Na. The patterns in these two quantities can more easily be seen by plotting energy against the number of electrons in each reactant, as shown in **Figure 14** for electron affinity and first and second ionization energy.

The peaks and valleys match for all three graphs because the electron configurations match—for example, there are peaks at 10 electrons and valleys at 11 electrons. At 10 electrons, all three reactant species (F^-, Ne, and Na^+) have identical $1s^2 2s^2 2p^6$ configurations; these are by definition isoelectronic species. The relatively high energy necessary to remove an electron from these configurations is typical for configurations in which electron shells are complete. The next electron, in an 11-electron configuration, is the first to occupy a higher energy $3s$ orbital and is much more easily lost, providing a valley in each graph, corresponding to removal of an electron from the 11-electron species Ne^-, Na, and Mg^+.

EXERCISE 8

Explain why all three graphs in Figure 14 have maxima at 4 electrons and minima at 5 electrons.

3.3 Covalent and Ionic Radii

The sizes of atoms and ions are also related to the ionization energies and electron affinities. As the nuclear charge increases, the electrons are pulled in toward the center of the atom, and the size of any particular orbital decreases. On the other hand, as the nuclear charge increases, more electrons are added to the atom, and their mutual repulsion keeps the outer orbitals large. The interaction of these two effects, increasing nuclear charge and increasing number of electrons, results in a gradual decrease in atomic size across each period. **Table 8** gives nonpolar covalent radii, based on bond distances in nonpolar molecules. There are other measures of atomic size, such as the van der Waals radius, in which collisions with other atoms are used to define the size. It is difficult to obtain consistent data for any such measure, because the polarity, chemical structure, and physical state of molecules change drastically from one compound to another. The numbers shown here are sufficient for a general comparison of different elements.

There are similar challenges in determining the size of ions. Because the stable ions of the different elements have different charges and different numbers of electrons, as well as different crystal structures for their compounds, it is difficult to find a suitable set of numbers for comparison. Earlier data were based on Pauling's approach, in which the ratio of the radii of isoelectronic ions was assumed to be equal to the ratio of their effective

TABLE 8 Nonpolar Covalent Radii (pm)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
32																	31
Li	Be											B	C	N	O	F	Ne
123	89											82	77	75	73	71	69
Na	Mg											Al	Si	P	S	Cl	Ar
154	136											118	111	106	102	99	98
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
203	174	144	132	122	118	117	117	116	115	117	125	126	122	120	117	114	111
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
216	191	162	145	134	130	127	125	125	128	134	148	144	140	140	136	133	126
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Ra
235	198	169	144	134	130	128	126	127	130	134	149	148	147	146	(146)	(145)	

Source: Data from R. T. Sanderson, *Inorganic Chemistry*, Reinhold, New York, 1967, p. 74; and E. C. M. Chen, J. G. Dojahn, W. E. Wentworth, *J. Phys. Chem. A*, **1997**, *101*, 3088.

TABLE 9 Crystal Radii for Selected Ions

	Z	Element	Radius (pm)
Alkali metal ions	3	Li^+	90
	11	Na^+	116
	19	K^+	152
	37	Rb^+	166
	55	Cs^+	181
Alkaline earth ions	4	Be^{2+}	59
	12	Mg^{2+}	86
	20	Ca^{2+}	114
	38	Sr^{2+}	132
	56	Ba^{2+}	149
Other cations	13	Al^{3+}	68
	30	Zn^{2+}	88
Halide ions	9	F^-	119
	17	Cl^-	167
	35	Br^-	182
	53	I^-	206
Other anions	8	O^{2-}	126
	16	S^{2-}	170

Source: Data from R. D. Shannon, *Acta Crystallogr*. **1976**, *A32*, 751 for six-coordinate ions.

nuclear charges. More recent calculations are based on a number of considerations, including electron density maps from X-ray data that show larger cations and smaller anions than those previously found. Those in **Table 9** were called "crystal radii"

by Shannon[22] and are generally different from the older values of "ionic radii" by +14 pm for cations and –14 pm for anions, as well as being revised to accommodate more recent measurements. The radii in Table 9 can be used for rough estimation of the packing of ions in crystals and other calculations, as long as the "fuzzy" nature of atoms and ions is kept in mind.

Factors that influence ionic size include the coordination number of the ion, the covalent character of the bonding, distortions of regular crystal geometries, and delocalization of electrons (metallic or semiconducting character. The radius of the anion is also influenced by the size and charge of the cation. Conversely, the anion exerts a smaller influence on the radius of the cation.[23]

The values in **Table 10** show that anions are generally larger than cations with similar numbers of electrons. The radius decreases as nuclear charge increases for ions with the same electronic structure, with the charge on cations having a strong effect, for example in the series Na^+, Mg^{2+}, Al^{3+}. Within a group, the ionic radius increases as Z increases because of the larger number of electrons in the ions and, for the same element, the radius decreases with increasing charge on the cation. Examples of these trends are shown in Tables 10, **11**, and **12**.

TABLE 10 Crystal Radius and Nuclear Charge

Ion	Protons	Electrons	Radius (pm)
O^{2-}	8	10	126
F^-	9	10	119
Na^+	11	10	116
Mg^{2+}	12	10	86
Al^{3+}	13	10	68

TABLE 11 Crystal Radius and Total Number of Electrons

Ion	Protons	Electrons	Radius (pm)
O^{2-}	8	10	126
S^{2-}	16	18	170
Se^{2-}	34	36	184
Te^{2-}	52	54	207

TABLE 12 Crystal Radius and Ionic Charge

Ion	Protons	Electrons	Radius (pm)
Ti^{2+}	22	20	100
Ti^{3+}	22	19	81
Ti^{4+}	22	18	75

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General References

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Problems

1 Determine the de Broglie wavelength of
- **a.** an electron moving at 1/10 the speed of light.
- **b.** a 400 g Frisbee moving at 10 km/h.
- **c.** an 8.0-pound bowling ball rolling down the lane with a velocity of 2.0 meters per second.
- **d.** a 13.7 g hummingbird flying at a speed of 30.0 miles per hour.

2 Using the equation $E = R_H\left(\frac{1}{2^2} - \frac{1}{n_h^2}\right)$, determine the energies and wavelengths of the visible emission bands in the atomic spectrum of hydrogen arising from $n_h = 4$, 5, and 6. (The red line, corresponding to $n_h = 3$, was calculated in Exercise 1.)

3 The transition from the $n = 7$ to the $n = 2$ level of the hydrogen atom is accompanied by the emission of radiation slightly beyond the range of human perception, in the ultraviolet region. Determine the energy and wavelength.

4 Emissions are observed at wavelengths of 383.65 and 379.90 nm for transitions from excited states of the hydrogen atom to the $n = 2$ state. Determine the quantum numbers n_h for these emissions.

5 What is the least amount of energy that can be emitted by an excited electron in a hydrogen atom falling from an excited state directly to the $n = 3$ state? What is the quantum number n for the excited state? Humans cannot visually observe the photons emitted in this process. Why not?

6 Hydrogen atom emission spectra measured from the solar corona indicated that the 4*s* orbital was 102823.8530211 cm^{-1}, and 3*s* orbital 97492.221701 cm^{-1}, respectively, above the 1*s* ground state. (These energies have tiny uncertainties, and can be treated as exact numbers for the sake of this problem.) Calculate the difference in energy (J) between these levels on the basis of these data, and compare this difference to that

obtained by the Balmer equation in Section 1.2. How well does the Balmer equation work for hydrogen? (Data from Y. Ralchenko, A. E. Kramida, J. Reader, and NIST ASD Team (2011). *NIST Atomic Spectra Database* (ver. 4.1.0), [Online]. Available: http:// physics.nist.gov/asd [2012, January 18]. National Institute of Standards and Technology, Gaithersburg, MD.)

7 The Rydberg constant equation has two terms that vary depending on the species under consideration, the reduced mass of the electron/nucleus combination and the charge of the nucleus (Z).

a. Determine the approximate *ratio* between the Rydberg constants for isoelectronic He^+ (consider the most abundant helium-4 isotope) and H.

b. Use this ratio to calculate an approximate Rydberg constant (J) for He^+.

c. The difference between the He^+ $2s$ and $1s$ orbitals was reported as 329179.76197(20) cm^{-1}. Calculate the He^+ Rydberg constant from this spectral line for comparison to your value from **b.**
(Data from the same reference as Problem 6.)

8 The details of several steps in the particle-in-a-box model in this chapter have been omitted. Work out the details of the following steps:

a. Show that if $\Psi = A \sin rx + B \cos sx$ (A, B, r, and s are constants) is a solution to the wave equation for the one-dimensional box, then

$$r = s = \sqrt{2mE}\left(\frac{2\pi}{h}\right)$$

b. Show that if $\Psi = A \sin rx$, the boundary conditions ($\Psi = 0$ when $x = 0$ and $x = a$) require that $r = \pm \dfrac{n\pi}{a}$, where $n =$ any integer other than zero.

c. Show that if $r = \pm \dfrac{n\pi}{a}$, the energy levels of the particle are given by $E = \dfrac{n^2h^2}{8ma^2}$

d. Show that substituting the value of r given in part c into $\Psi = A \sin rx$ and applying the normalizing requirement gives $A = \sqrt{2/a}$.

9 For the $3p_z$ and $4d_{xz}$ hydrogen-like atomic orbitals, sketch the following:

a. The radial function R

b. The radial probability function $a_0 r^2 R^2$

c. Contour maps of electron density.

10 Repeat the exercise in Problem 9, for the $4s$ and $5d_{x^2-y^2}$ orbitals.

11 Repeat the exercise in Problem 9, for the $5s$ and $4d_{z^2}$ orbitals.

12 The $4f_{z(x^2-y^2)}$ orbital has the angular function $Y = (\text{constant})\, z(x^2 - y^2)/r^3$.

a. How many radial nodes does this orbital have?

b. How many angular nodes does it have?

c. Write equations to define the angular nodal surfaces. What shapes are these surfaces?

d. Sketch the shape of the orbital, and show all radial and angular nodes.

13 Repeat the exercise in Problem 12, for the $5f_{xyz}$ orbital, which has $Y = (\text{constant})\, xyz/r^3$.

14 The label for an f_{z^3} orbital, like that for a d_{z^2} orbital, is an abbreviation. The actual angular function for this orbital is $Y = (\text{constant}) \times z(5z^2 - 3r^2)/r^3$. Repeat the exercise in Problem 12, for a $4f_{z^3}$ orbital. (*Note*: recall that $r^2 = x^2 + y^2 + z^2$).

15 **a.** Determine the possible values for the l and m_l quantum numbers for a $5d$ electron, a $4f$ electron, and a $7g$ electron.

b. Determine the possible values for all four quantum numbers for a $3d$ electron.

c. What values of m_l are possible for f orbitals?

d. At most, how many electrons can occupy a $4d$ orbital?

16 **a.** What are the values of quantum numbers l and n for a $5d$ electron?

b. At most, how many $4d$ electrons can an atom have? Of these electrons how many, at most, can have $m_s = -\frac{1}{2}$?

c. A $5f$ electron has what value of quantum number l? What values of m_l may it have?

d. What values of the quantum number m_l are possible for a subshell having $l = 4$?

17 **a.** At most, how many electrons in an atom can have both $n = 5$ and $l = 3$?

b. A $5d$ electron has what possible values of the quantum number m_l?

c. What value of quantum number l do p orbitals have? For what values of n do p orbitals occur?

d. What is the quantum number l for g orbitals? How many orbitals are in a g subshell?

18 Determine the Coulombic and exchange energies for the following states, and determine which state is favored (has lower energy):

a. ___↑___ ___↑___ and ___↑ ↓___ _____

b. ___↑___ ___↑___ ___↑___ and ___↑ ↓___ ___↑___ _____

19 Two excited states for a d^4 configuration are shown. Which is likely to have lower energy? Explain your choice in terms of Coulombic and exchange energies.

W: ___↑___ ___↑___ ___↓___ ___↓___ _____

X: ___↑___ ___↑___ ___↑___ ___↓___ _____

20 Two excited states for a d^5 configuration are shown. Which is likely to have lower energy? Why? Explain your choice in terms of Coulombic and exchange energies.

Y: ___↑___ ___↑___ ___↑___ ___↓___ ___↓___

Z: ___↑___ ___↑___ ___↑___ ___↑___ ___↓___

21 What states are possible for a d^3 configuration? Determine the Coulombic and exchange energies for each, and rank the states in terms of relative energy.

22 Provide explanations of the following phenomena:
- **a.** The electron configuration of Cr is [Ar] $4s^1 3d^5$ rather than [Ar] $4s^2 3d^4$.
- **b.** The electron configuration of Ti is [Ar] $4s^2 3d^2$, but that of Cr^{2+} is [Ar] $3d^4$.

23 Give electron configurations for the following:
- **a.** V
- **b.** Br
- **c.** Ru^{3+}
- **d.** Hg^{2+}
- **e.** Sb

24 Predict the electron configurations of the following metal anions:
- **a.** Rb^-
- **b.** Pt^{2-} (See: A. Karbov, J. Nuss, U. Weding, M. Jansen, *Angew. Chem. Int. Ed.*, **2003**, *42*, 4818.)

25 Radial probability plots shed insight on issues of shielding and effective nuclear charge. Interpret the radial probability functions in Figure 7 to explain why the general order of orbital filling is $n = 1$, followed by $n = 2$, followed by $n = 3$. Interpret the graphs for $3s$, $3p$, and $3d$ to rationalize the filling order for these orbitals.

26 Briefly explain the following on the basis of electron configurations:
- **a.** Fluorine forms an ion having a charge of 1–.
- **b.** The most common ion formed by zinc has a 2+ charge.
- **c.** The electron configuration of the molybdenum atom is [Kr] $5s^1\ 4d^5$ rather than [Kr] $5s^2\ 4d^4$.

27 Briefly explain the following on the basis of electron configurations:
- **a.** The most common ion formed by silver has a 1+ charge.
- **b.** Cm has the outer electron configuration $s^2 d^1 f^7$ rather than $s^2 f^8$.
- **c.** Sn often forms an ion having a charge of 2+ (the *stannous* ion).

28
- **a.** Which 2+ ion has two $3d$ electrons? Which has eight $3d$ electrons?
- **b.** Which is the more likely configuration for Mn^{2+}: [Ar] $4s^2 3d^3$ or [Ar] $3d^5$?

29 Using Slater's rules, determine Z^* for
- **a.** a $3p$ electron in P, S, Cl, and Ar. Is the calculated value of Z^* consistent with the relative sizes of these atoms?
- **b.** a $2p$ electron in O^{2-}, F^-, Na^+ and Mg^{2+}. Is the calculated value of Z^* consistent with the relative sizes of these ions?
- **c.** a $4s$ and a $3d$ electron of Cu. Which type of electron is more likely to be lost when copper forms a positive ion?
- **d.** a $4f$ electron in Ce, Pr, and Nd. There is a decrease in size, commonly known as the **lanthanide contraction,** with increasing atomic number in the lanthanides. Are your values of Z^* consistent with this trend?

30 A sample calculation in this chapter showed that, according to Slater's rules, a $3d$ electron of nickel has a higher effective nuclear charge than a $4s$ electron. Is the same true for early first-row transition metals? Using Slater's rules, calculate S and Z^* for $4s$ and $3d$ electrons of Sc and Ti, and comment on the similarities or differences with Ni.

31 Ionization energies should depend on the effective nuclear charge that holds the electrons in the atom. Calculate Z^* (Slater's rules) for N, P, and As. Do their ionization energies seem to match these effective nuclear charges? If not, what other factors influence the ionization energies?

32 Prepare a diagram such as the one in Figure 12(a) for the fifth period in the periodic table, elements Zr through Pd. The configurations in Table 7 can be used to determine the crossover points of the lines. Can a diagram be drawn that is completely consistent with the configurations in the table?

33 Why are the ionization energies of the alkali metals in the order Li >, Na > K > Rb?

34 The second ionization of carbon ($C^+ \longrightarrow C^{2+} + e^-$) and the first ionization of boron ($B \longrightarrow B^+ + e^+$) both fit the reaction $1s^2 2s^2 2p^1 \longrightarrow 1s^2 2s^2 + e^-$. Compare the two ionization energies (24.383 eV and 8.298 eV, respectively) and the effective nuclear charge Z^*. Is this an adequate explanation of the difference in ionization energies? If not, suggest other factors.

35 Explain why all three graphs in Figure 14 have maxima at 4 electrons and minima at 5 electrons.

36
- **a.** For a graph of third ionization energy against atomic number, predict the positions of peaks and valleys for elements through atomic number 12. Compare the positions of these peaks and valleys with those for first ionization energies shown in Figure 13.
- **b.** How would a graph of third ionization energies against the number of electrons in reactant compare with the other graphs shown in Figure 14? Explain briefly.

37 The second ionization energy involves removing an electron from a positively charged ion in the gas phase (see preceding problem). How would a graph of second ionization energy vs. atomic number for the elements helium through neon compare with the graph of first ionization energy in Figure 13? Be specific in comparing the positions of peaks and valleys.

38 In each of the following pairs, pick the element with the higher ionization energy and explain your choice.
- **a.** Fe, Ru
- **b.** P, S
- **c.** K, Br
- **d.** C, N
- **e.** Cd, In
- **f.** Cl, F

39 On the basis of electron configurations, explain why
- **a.** sulfur has a lower electron affinity than chlorine.
- **b.** iodine has a lower electron affinity than bromine.
- **c.** boron has a lower ionization energy than beryllium.
- **d.** sulfur has a lower ionization energy than phosphorus.

40 **a.** The graph of ionization energy versus atomic number for the elements Na through Ar (Figure 13) shows maxima at Mg and P and minima at Al and S. Explain these maxima and minima.

b. The graph of electron affinity versus atomic number for the elements Na through Ar (Figure 13) also shows maxima and minima, but shifted by one element in comparison with the ionization energy graph. Why are the maxima and minima shifted in this way?

41 The second ionization energy of He is almost exactly four times the ionization energy of H, and the third ionization energy of Li is almost exactly nine times the ionization energy of H:

	IE (MJ mol^{-1})
$H(g) \longrightarrow H^+(g) + e^-$	1.3120
$He^+(g) \longrightarrow He^{2+}(g) + e^-$	5.2504
$Li^{2+}(g) \longrightarrow Li^{3+}(g) + e^-$	11.8149

Explain this trend on the basis of the Bohr equation for energy levels of single-electron systems.

42 The size of the transition-metal atoms decreases slightly from left to right in the periodic table. What factors must be considered in explaining this decrease? In particular, why does the size decrease at all, and why is the decrease so gradual?

43 Predict the largest and smallest radius in each series, and account for your choices:

a. Se^{2-} Br^- Rb^+ Sr^{2+}

b. Y^{3+} Zr^{4+} Nb^{5+}

c. Co^{4+} Co^{3+} Co^{2+} Co

44 Select the best choice, and briefly indicate the reason for each choice:

a. Largest radius: Na^+ Ne F^-

b. Greatest volume: S^{2-} Se^{2-} Te^{2-}

c. Highest ionization energy: Na Mg Al

d. Most energy necessary to remove an electron: Fe Fe^{2+} Fe^{3+}

e. Highest electron affinity: O F Ne

45 Select the best choice, and briefly indicate the reason for your choice:

a. Smallest radius: Sc Ti V

b. Greatest volume: S^{2-} Ar Ca^{2+}

c. Lowest ionization energy: K Rb Cs

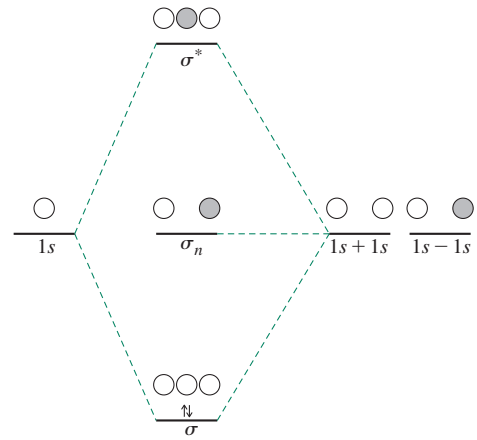
d. Highest electron affinity: Cl Br I

e. Most energy necessary to remove an electron: Cu Cu^+ Cu^{2+}

46 There are a number of Web sites that display atomic orbitals. Use a search engine to find a complete set of the *f* orbitals.
- **a.** How many orbitals are there in one set (for example, a set of 4*f* orbitals)?
- **b.** Describe the angular nodes of the orbitals.
- **c.** Observe what happens to the number of radial nodes as the principal quantum number is increased.
- **d.** Include the URL for the site you used for each, along with sketches or printouts of the orbitals. (Two useful Web sites at this writing are orbitals.com and winter.group.shef.ac.uk/orbitron.)

47 Repeat the exercise in Problem 46, this time for a set of *g* orbitals.

Answers to Exercises



1 $$E = R_H\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = R_H\left(\frac{5}{36}\right) = 2.179 \times 10^{-18}\ \text{J}\left(\frac{5}{36}\right) = 3.026 \times 10^{-19}\ \text{J}$$

$$= 1.097 \times 10^{7}\ \text{m}^{-1}\left(\frac{5}{36}\right) = 1.524 \times 10^{6}\ \text{m}^{-1} \times \frac{\text{m}}{100\ \text{cm}} = 1.524 \times 10^{4}\ \text{cm}^{-1}$$

2 The nodal surfaces require $2z^2 - x^2 - y^2 = 0$, so the angular nodal surface for a d_{z^2} orbital is the conical surface where $2z^2 = x^2 + y^2$.

3 The angular nodal surfaces for a d_{xz} orbital are the planes where $xz = 0$, which means that either x or z must be zero. The yz and xy planes satisfy this requirement.

4 ↑↓ ↑ ↓ One pair with ↑ spin, one pair with ↓ spin, one exchange possibility for each; energy contribution $2\Pi_e$. One pair (first orbital), energy contribution Π_c. Total: $2\Pi_e + \Pi_c$

↑↓ ↑↓ — $2\Pi_e + 2\Pi_c$

Π_c

↑↓ ↑ ↓ $2\Pi_e + \Pi_c$

Π_e

↑↓ ↑ ↑ $3\Pi_e + \Pi_c$

5 **a.** If the three $2p$ electrons all have the same spin, as in ↑1 ↑2 ↑3, there are three exchange possibilities (1 and 2, 1 and 3, or 2 and 3) and no pairs. Overall, the total energy is $3\Pi_e$. If there is one unpaired electron, as in ↑↓ ↑ —, there is one electron with ↓ spin, and no possibility of exchange; two electrons with ↑ spin, with one exchange possibility; and one pair. Overall; the total energy is $\Pi_e + \Pi_c$. Because Π_e is negative and Π_c is positive, the configuration with three unpaired electrons has a much lower energy.

b. If the three $2p$ electrons avoid pairing, but do not all have mutually parallel spins, as in ↑ ↑ ↓, only the two ↑ electrons can exchange. The total energy is Π_e. The energy of this state is intermediate between those in part a. It is $2\Pi_e$ higher than ↑ ↑ ↑ and lower than ↑↓ ↑ — by Π_c.

6

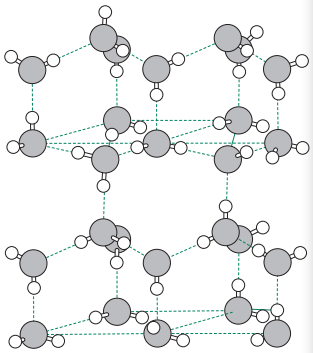
Tin	Total	5*p*	5*s*	4*d*
Z	**50**	**50**	**50**	**50**
($1s^2$)	2	2	2	2
($2s^2 2p^6$)	8	8	8	8
($3s^2 3p^6$)	8	8	8	8
($3d^{10}$)	10	10	10	10
($4s^2 4p^6$)	8	8 × 0.85	8 × 0.85	8
($4d^{10}$)	10	10 × 0.85	10 × 0.85	9 × 0.35
($5s^2 5p^2$)	4	3 × 0.35	3 × 0.35	
Z^*		5.65	5.65	10.85

7

Uranium	Total	7*s*	5*f*	6*d*
Z	**92**	**92**	**92**	**92**
($1s^2$)	2	2	2	2
($2s^2 2p^6$)	8	8	8	8
($3s^2 3p^6$)	8	8	8	8
($3d^{10}$)	10	10	10	10
($4s^2 4p^6$)	8	8	8	8
($4d^{10}$)	10	10	10	10
($4f^{14}$)	14	14	14	14
($5s^2 5p^6$)	8	8	8	8
($5d^{10}$)	10	10	10	10
($5f^3$)	3	3	2 × 0.35	3
($6s^2 6p^6$)	8	8 × 0.85		8
($6d^1$)	1	1 × 0.85		
($7s^2$)	2	1 × 0.35		
Z^*		3.00	13.30	3.00

8 With 4 electrons, the electron configurations of B^+, Be, and Li^- are all $1s^2\,2s^2$. Because the effective nuclear charge is greater for each $1s^2\,2s^2$ configuration than the $1s^2\,2s^1$ configuration of the preceding element, more energy is necessary to remove an electron from the species with $1s^2\,2s^2$ configurations. For 5 electrons (C^+, B, and Be^-) the configurations are all $1s^2\,2s^2\,2p^1$. Because the 2*p* orbitals are significantly higher in energy than the 2*s* orbitals, in each case it is much easier to remove an electron from a $1s^2\,2s^2\,2p^1$ configuration than from the $1s^2\,2s^2$ configuration of the preceding element. When a sixth electron is present (a $1s^2\,2s^2\,2p^2$ configuration), more energy is required to remove an electron because the electron being removed must overcome greater effective nuclear charge than for the preceding 5-electron species.

Simple Bonding Theory



We now turn from the use of quantum mechanics and its description of the atom to an elementary description of molecules. Although most of our discussion of chemical bonding uses the molecular orbital approach, less rigorous methods that provide approximate pictures of the shapes and polarities of molecules are also useful. This chapter provides an overview of Lewis dot structures, valence shell electron-pair repulsion (VSEPR), and related topics. The ideas of this chapter provide a starting point for molecular orbital descriptions.

Ultimately, any description of bonding must be consistent with experimental data on bond lengths, bond angles, and bond strengths. Angles and distances are most frequently determined by diffraction (X-ray crystallography, electron diffraction, neutron diffraction) or spectroscopic (microwave, infrared) methods. For many molecules, there is general agreement on the nature of the bonding, although there are alternative ways to describe it. For others, there is considerable difference of opinion on the best way to describe the bonding. In this chapter we describe some useful qualitative approaches, including some of the opposing views.

1 Lewis Electron-Dot Diagrams

Lewis electron-dot diagrams, although oversimplified, provide a good starting point for analyzing the bonding in molecules. Credit for their initial use goes to G. N. Lewis,[1] an American chemist who contributed much to the understanding of thermodynamics and chemical bonding in the early twentieth century. In Lewis diagrams, bonds between two atoms exist when they share one or more pairs of electrons. In addition, some molecules have nonbonding pairs, also called *lone pairs*, of electrons on atoms. These electrons contribute to the shape and reactivity of the molecule but do not directly bond the atoms together. Most Lewis structures are based on the concept that eight **valence electrons**, corresponding to *s* and *p* electrons outside the noble gas core, form a particularly stable arrangement, as in the noble gases with $s^2\,p^6$ configurations. An exception is hydrogen, which is stable with two valence electrons. Also, some molecules require more than eight electrons around a given central atom, and some molecules require fewer than eight electrons.

Simple molecules such as water follow the **octet rule**, in which eight electrons surround the central atom. Each hydrogen atom shares two electrons with the oxygen, forming the familiar structure with two bonds; the O atom accommodates two bonding pairs and two lone pairs:*

*The treatment of water via molecular orbital theory results in an electronic structure in which each of these electron pairs has a unique energy. This model is supported by spectroscopic evidence, and indicates one limitation of the Lewis model.

Shared electrons are considered to contribute to the electronic requirements of both atoms involved; thus, the electron pairs shared by H and O in the water molecule are counted toward both the 8-electron requirement of oxygen and the 2-electron requirement of hydrogen.

The Lewis model defines double bonds as containing four electrons and triple bonds as containing six electrons:

1.1 Resonance

In many Lewis structures, the choice of which atoms are connected by multiple bonds is arbitrary. When alternate locations for single bonds and multiple bonds are possible that all afford valid Lewis structures, a structure demonstrating each option should be drawn. For example, three drawings (resonance structures) of CO_3^{2-} are needed (**Figure 1**) to show the double bond in each of the three possible C—O positions. In fact, experimental evidence shows that all three C—O bonds are equivalent, with bond lengths (129 pm) between typical C—O double-bond and single-bond distances (116 pm and 143 pm, respectively). All three drawings are necessary to describe the structure, with each drawing contributing equally to describe the bonding in the actual ion. This is called **resonance**; there is more than one possible way in which the valence electrons can be placed in a Lewis structure. Note that in resonance structures, such as those shown for CO_3^{2-} in Figure 1, the electrons are arranged differently, but the nuclei remain in fixed positions.

The species CO_3^{2-} and NO_3^- have the same number of electrons (*i.e.*, they are **isoelectronic**) and use the same orbitals for bonding. Their Lewis diagrams are identical except for the identity and formal charge (Section 1.3) of the central atom.

When a molecule has several resonance structures, its overall electronic energy is lowered, making it more stable. Just as the energy levels of a particle in a box are lowered by making the box larger, the electronic energy levels of the bonding electrons are lowered when the electrons can occupy a larger space.

1.2 Higher Electron Counts

When it is impossible to draw a structure consistent with the octet rule because additional valence electrons remain to be assigned after the octet rule is satisfied on all atoms, it is necessary to increase the number of electrons around the central atom. An option limited to elements of the third and higher periods is to use *d* orbitals for this expansion, although theoretical work suggests that expansion beyond the *s* and *p* orbitals is unnecessary for most main group molecules.[2] In most cases, two or four added electrons will complete the bonding, but more can be added if necessary. For example, 10 electrons are required around chlorine in ClF_3 and 12 around sulfur in SF_6 (**Figure 2**). The increased number of electrons is often described as an *expanded shell* or an *expanded electron count*. The term **hypervalent** is used to describe central atoms that have electron counts greater than the atom's usual requirement.

There are examples with even more electrons around the central atom, such as IF_7 (14 electrons), $[TaF_8]^{3-}$ (16 electrons), and $[XeF_8]^{2-}$ (18 electrons). There are rarely more than 18 electrons (2 for *s*, 6 for *p*, and 10 for *d* orbitals) around a single atom in the top half of the periodic table, and crowding of the outer atoms usually keeps the number below this, even for much heavier atoms that have *f* orbitals energetically available.

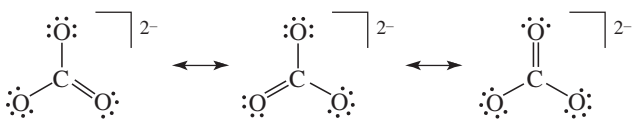


FIGURE 1 Lewis Diagrams for CO_3^{2-}.

1.3 Formal Charge

Formal charge is the apparent electronic charge of each atom in a molecule, based on the electron-dot structure. Formal charges help assess resonance structures and molecular topology, and they are presented here as a simplified method of describing structures, just as the Bohr model is a simple method of describing electronic configurations in atoms. Both of these methods have limitations, and other approaches are more accurate, but they can be useful as long as their imperfections are kept in mind.

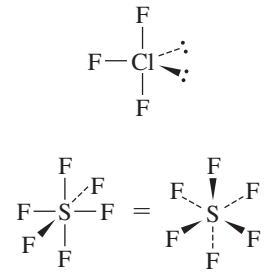


FIGURE 2 Structures of ClF_3 and SF_6.

Formal charges can help in eliminating resonance structures expected to contribute very little to the electronic ground state of the molecule, and, in some cases, suggesting multiple bonds beyond those required by the octet rule. It is essential, however, to remember that formal charge is only a tool for assessing Lewis structures, not a measure of any actual charge on the atoms. The number of valence electrons available in a free atom of an element minus the total for that atom in the molecule—determined by counting lone pairs as two electrons and bonding pairs as one electron assigned to each atom—is the formal charge on the atom:

$$\text{Formal charge} = \begin{pmatrix}\text{number of valence}\\ \text{electrons in a free}\\ \text{atom of the element}\end{pmatrix} - \begin{pmatrix}\text{number of unshared}\\ \text{electrons on the atom}\end{pmatrix} - \begin{pmatrix}\text{number of bonds}\\ \text{to the atom}\end{pmatrix}$$

In addition,

$$\text{Charge on molecule or ion} = \text{sum of formal charges}$$

Resonance structures that contribute more to the electronic ground state of the species generally (a) have smaller magnitudes of formal charges, (b) place negative formal charges on more electronegative elements (in the upper right-hand part of the periodic table), and (c) have smaller separation of charges. Three examples—SCN^-, OCN^-, and CNO^-—will illustrate the use of formal charges in describing electronic structures.

EXAMPLE 1

SCN^-

In the thiocyanate ion, SCN^-, three resonance structures are consistent with the electron-dot method, as shown in **Figure 3**. Structure A has only one negative formal charge on the nitrogen atom, the most electronegative atom in the ion. Structure B has a single negative charge on the S, which is less electronegative than N. Structure C has charges of 2− on N and 1+ on S, consistent with the relative electronegativities of these atoms but also has a large magnitude 2− charge and greater charge separation than the other structures. Therefore these structures lead to the prediction that structure A contributes the most to the electronic ground state of SCN^-, structure B contributes an intermediate amount, and any contribution from C is minor in describing the electronic ground state of SCN^-.

The bond lengths in **Table 1** are somewhat consistent with this conclusion, with SCN^- bond lengths between those of structures A and B. Protonation of the ion forms HNCS, consistent with a negative charge on N in SCN^-. The bond lengths in HNCS are close to those of double bonds, consistent with the structure H—N=C=S.

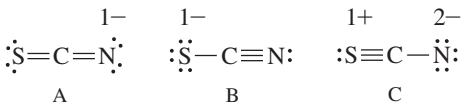


FIGURE 3 Resonance Structures of Thiocyanate, SCN^-.

TABLE 1 Table of S—C and C—N Bond Lengths (pm)

	S—C	C—N
SCN^- (in NaSCN)	165	118
HNCS	156	122
Single bond	181	147
Double bond	155	128 (approximate)
Triple bond		116

Data from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, New York, 1984, pp. 807, 926, 934–936.

EXAMPLE 2

OCN^-

The isoelectronic cyanate ion, OCN^- (**Figure 4**), has the same possibilities, but the larger electronegativity of O is expected to make structure B contribute more to the electronic ground state in cyanate relative the contribution of B in thiocyanate. The protonation of cyanate results in two isomers, 97% HNCO and 3% HOCN, consistent with a major contribution of structure A and a small, but significant, contribution from B. The bond lengths in OCN^- and HNCO in **Table 2** are reasonably consistent with this analysis. Formal charge arguments provide a good starting point to assess Lewis structures, and reactivity patterns are also useful to gain experimental insight about electron distributions.

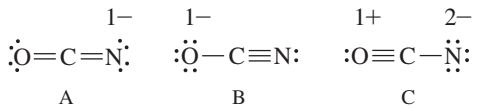


FIGURE 4 Resonance Structures of Cyanate, OCN^-.

TABLE 2 Table of O—C and C—N Bond Lengths (pm)

	O—C	C—N
OCN^-	126	117
HNCO	118	120
Single bond	143	147
Double bond	116 (CO_2)	128 (approximate)
Triple bond	113 (CO)	116

Data from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, New York, 1984, pp. 807, 926, 933–934; S. E. Bradforth, E. H. Kim, E. W. Arnold, D. M. Neumark, *J. Chem. Phys.*, **1993**, *98*, 800.

EXAMPLE 3

CNO^-

The isomeric fulminate ion, CNO^- (**Figure 5**), can be drawn with three similar structures, but the resulting formal charges have larger magnitudes than in OCN^-. Because the order of electronegativities is C < N < O, none of these are ideal structures, and it is not surprising that this ion is unstable. The only common fulminate salts are of mercury and silver; both are explosive. Fulminic acid is linear HCNO in the vapor phase, consistent with the greatest contribution from structure C; coordination complexes of CNO^- with transition-metal ions are known with MCNO structures.[3]

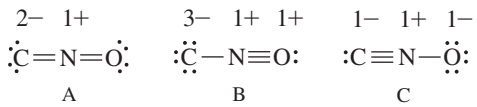


FIGURE 5 Resonance Structures of Fulminate, CNO^-.

EXERCISE 1 Use electron-dot diagrams and formal charges to predict the bond order for each bond in POF_3, SOF_4, and SO_3F^-.

Some molecules have satisfactory electron-dot structures with octets but have more reasonable formal charge distributions in their structures with expanded electron counts. In each of the cases in **Figure 6**, the actual molecules and ions are consistent with electron counts greater than 8 on the central atom and with a large contribution from the resonance structure that uses multiple bonds to minimize formal charges. The multiple bonds may also influence the shapes of the molecules.

1.4 Multiple Bonds in Be and B Compounds

A few molecules—such as BeF_2, $BeCl_2$, and BF_3—seem to require multiple bonds to satisfy the octet rule for Be and B, even though multiple bonds for F and Cl are not generally expected on the basis of the high electronegativities of these halogens. Structures minimizing formal charges for these molecules have only four electrons in the valence shell of Be and six electrons in the valence shell of B, in both cases fewer than the usual octet. The alternative, requiring eight electrons on the central atom, predicts multiple bonds, with BeF_2 analogous to CO_2 and BF_3 analogous to SO_3 (**Figure 7**). These structures, however, result in nonideal formal charges (2− on Be and 1+ on F in BeF_2, and 1− on B and 1+ on the double-bonded F in BF_3) on the basis of the usual rules.

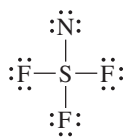
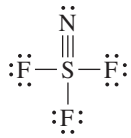
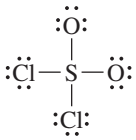
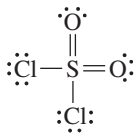
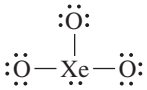
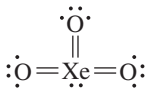
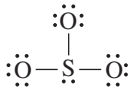
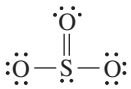
	Octet			*Expanded*			
Molecule		*Atom*	*Formal Charge*		*Atom*	*Formal Charge*	*Expanded to:*
SNF_3		S N	2+ 2−		S N	0 0	12
SO_2Cl_2		S O	2+ 1−		S O	0 0	12
XeO_3		Xe O	3+ 1−		Xe O	0 0	14
SO_3^{2-}		S O	1+ 1−		S O	0 0,1−	10

FIGURE 6 Formal Charge and Expanded Electron Counts on Central Atom.

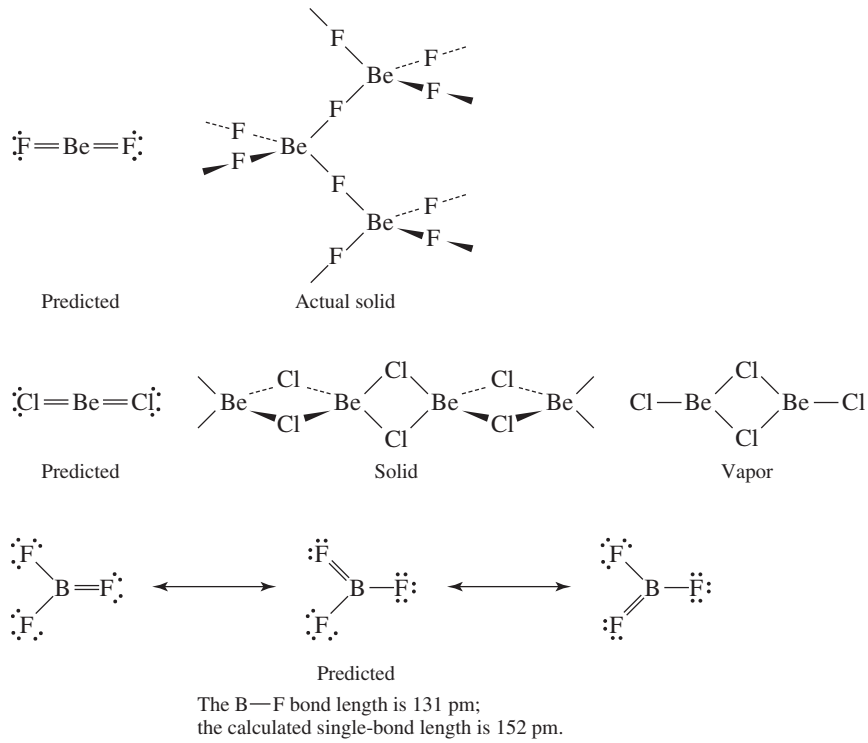


FIGURE 7 Structures of BeF_2, $BeCl_2$, and BF_3. (Data from A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, Oxford, England, 1984, pp. 412, 1047.)

In solid BeF_2, a complex network is formed with a Be atom coordination number of 4 (see Figure 7). $BeCl_2$ dimerizes to a 3-coordinate structure in the vapor phase, but the linear monomer is formed at high temperatures. This monomeric structure is unstable due to the electronic deficiency at Be; in the dimer and the network formed in the solid-state, the halogen atoms share lone pairs with the Be atom in an attempt to fill beryllium's valence shell. The monomer is still frequently drawn as a singly bonded structure, with only four electrons around the beryllium and the ability to accept lone pairs of other molecules to relieve its electronic deficiency (Lewis acid behavior).

Bond lengths in all the boron trihalides are shorter than expected for single bonds, so the partial double-bond character predicted seems reasonable despite the nonideal formal charges of these resonance forms. While a small amount of double bonding is possible in these molecules, the strong polarity of the B–halogen bonds and the ligand close-packing (LCP) model (Section 2.4) have been used to account for the short bonds without the need to invoke multiple bonding. The boron trihalides combine readily with other molecules that can contribute a lone pair of electrons (Lewis bases), forming a roughly tetrahedral structure with four bonds:

Because of this tendency, boron trihalides are frequently drawn with only six electrons around the boron.

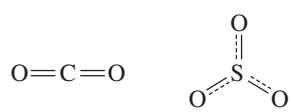
Other boron compounds that cannot be adequately described via simple electron-dot structures include hydrides such as B_2H_6, and many more complex molecules.

2 Valence Shell Electron-Pair Repulsion

Valence shell electron-pair repulsion (VSEPR) is an approach that provides a method for predicting the shape of molecules based on the electron-pair electrostatic repulsion described by Sidgwick and Powell[4] in 1940 and further developed by Gillespie and Nyholm[5] in 1957 and in the succeeding decades. Despite this method's simple approach, based on Lewis electron-dot structures, the VSEPR method in most cases predicts shapes that compare favorably with those determined experimentally. However, this approach at best provides approximate shapes for molecules. The most common method of determining the actual structures is X-ray diffraction, although electron diffraction, neutron diffraction, and many spectroscopic methods are also used.[6]

The basis of the VSEPR approach is that electrons repel each other because they are negatively charged. Quantum mechanical rules dictate that electrons can be accommodated in the same region of space as bonding pairs or lone pairs, but each pair repels all other pairs. According to the VSEPR model, therefore, molecules adopt geometries such that valence electron pairs position themselves as far from each other as possible to minimize electron–electron repulsions. A molecule can be described by the generic formula AX_mE_n, where *A* is the central atom, *X* stands for any atom or group of atoms surrounding the central atom, and *E* represents a lone pair of electrons. The **steric number*** **(SN = *m* + *n*)** is the total number of positions occupied by atoms or lone pairs around a central atom; lone pairs and bonding pairs both influence the molecular shape.

Carbon dioxide is a molecule with two atoms attached (SN = 2) to the central atom via double bonds. The electrons in each double bond must be between C and O, and the repulsion between these electron groups forces a linear structure on the molecule. Sulfur trioxide has three atoms bound to the sulfur (SN = 3), with equivalent partial double-bond character between sulfur and each oxygen, a conclusion rendered by analysis of its resonance forms. The best positions for the oxygens to minimize electron–electron repulsions in this molecule are at the corners of an equilateral triangle, with O—S—O bond angles of 120°. The multiple bonding does not affect the geometry, because all three bonds are equivalent in terms of bond order.



The same pattern of finding the Lewis structure and then matching it to a geometry that minimizes the repulsive energy of bonding electrons is followed through steric numbers 4, 5, 6, 7, and 8 where the outer atoms are identical in each molecule, as shown in **Figure 8**.

Bond angles and distances are uniform in each of these structures with two, three, four, and six electron pairs. Neither the corresponding 5- nor 7-coordinate structures can have uniform angles and distances, because there are no regular polyhedra with these numbers of vertices. The 5-coordinate molecules have a trigonal bipyramidal structure, with a central triangular plane of three positions plus two other positions above and below the center of the plane. The 7-coordinate molecules have a pentagonal bipyramidal structure, with a pentagonal plane of five positions and positions above and below the center of the plane. The regular square antiprism structure (SN = 8) is like a cube that has had the top face twisted 45° into the antiprism arrangement, as shown in **Figure 9**. It has three different bond angles for adjacent fluorines. $[TaF_8]^{3-}$ has square antiprismatic geometry but is distorted from this ideal in the solid.[7]

The steric number is also called the *number of electron pair domains*.

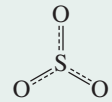
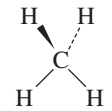
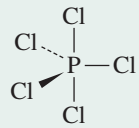
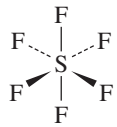
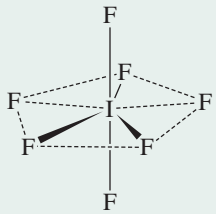
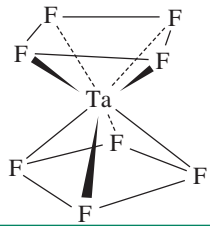
Steric Number	Geometry	Examples	Calculated Bond Angles	
2	Linear	CO_2	180°	O═C═O
3	Trigonal (triangular)	SO_3	120°	
4	Tetrahedral	CH_4	109.5°	
5	Trigonal bipyramidal	PCl_5	120°, 90°	
6	Octahedral	SF_6	90°	
7	Pentagonal bipyramidal	IF_7	72°, 90°	
8	Square antiprismatic	$[TaF_8]^{3-}$	70.5°, 99.6°, 109.5°	

FIGURE 8 VSEPR Predictions.

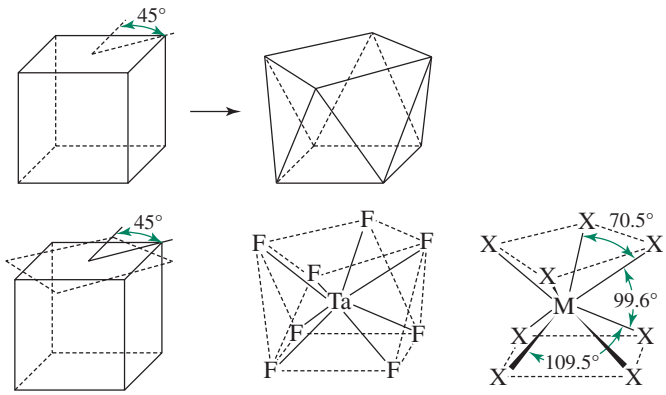


FIGURE 9 Conversion of a Cube into a Square Antiprism.

2.1 Lone-Pair Repulsion

Bonding models are useful only if their explanations are consistent with experimental data. New theories are continually being suggested and tested. Because we are working with such a wide variety of atoms and molecular structures, a single approach will unlikely work for all of them. Although the fundamental ideas of atomic and molecular structures are relatively simple, their application to complex molecules is not. To a first approximation, lone pairs, single bonds, double bonds, and triple bonds can all be treated similarly when predicting molecular shapes. However, better predictions of overall shapes can be made by considering some important differences between lone pairs and bonding pairs. These methods are sufficient to show the trends and explain the bonding, as in rationalizing why the H—N—H angle in ammonia is smaller than the tetrahedral angle in methane and larger than the H—O—H angle in water.

As a general guideline, the VSEPR model predicts that electron-pair repulsions involving lone pairs (*lp*) are stronger than those involving bonding pairs (*bp*) in the order

$$lp{-}lp \text{ repulsions} > lp{-}bp \text{ repulsions} > bp{-}bp \text{ repulsions}$$

Steric Number = 4

The isoelectronic molecules CH_4, NH_3, and H_2O (**Figure 10**) illustrate the effect of lone pairs on molecular shape. Methane has four identical bonds between carbon and each of the hydrogens. When the four pairs of electrons are arranged as far from each other as possible, the result is the familiar tetrahedral shape. The tetrahedron, with all H—C—H angles measuring 109.5°, has four identical bonds.

Ammonia also has four pairs of electrons around the central atom, but three are bonding pairs between N and H, and the fourth is a lone pair on the nitrogen. The nuclei form a trigonal pyramid with the three bonding pairs; the lone pair occupies the fourth region in space resulting in a tetrahedral arrangement of the four electron groups. Because each of the three bonding pairs is attracted by two positively charged nuclei (H and N), these pairs are largely confined to the regions between the H and N atoms. The lone pair, on the other hand, is attracted solely by the nitrogen nucleus; it has no second nucleus to confine it to a small region of space. Consequently, the lone pair tends to spread out and to occupy more space around the nitrogen than the bonding pairs. As a result, the H—N—H angles are 106.6°, nearly 3° smaller than the angles in methane.

The same principles apply to the water molecule, in which two lone pairs and two bonding pairs repel each other. Again, the electron pairs adopt a nearly tetrahedral arrangement, with the atoms arranged in a V shape. The angle of largest repulsion, between the two lone pairs, cannot be measured. However, the lone pair–bonding pair (*lp–bp*) repulsion is greater than the bonding pair–bonding pair (*bp–bp*) repulsion; as a result, the H—O—H bond angle is only 104.5°, another 2.1° decrease from the ammonia angles. The net result is that we can predict approximate molecular shapes by assigning more space to lone electron pairs; lone pairs are able to spread out and occupy more space since they are attracted to one nucleus rather than two.

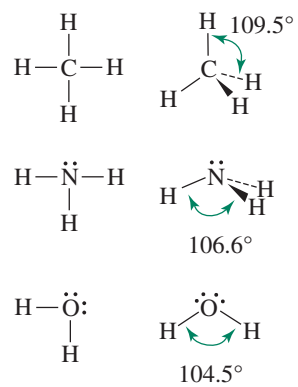


FIGURE 10 Shapes of Methane, Ammonia, and Water.

Steric Number = 5

For the trigonal bipyramidal geometry, there are two unique locations for electron pairs, axial and equatorial. If there is a single lone pair, for example in SF_4, the lone pair occupies an equatorial position. This position provides the lone pair with the most space and minimizes the interactions between the lone pair and bonding pairs. If the lone pair were axial, it would have three 90° interactions with bonding pairs; in an equatorial position, it has only two such interactions, as shown in **Figure 11**. The actual structure is distorted by the lone pair as it spreads out in space and effectively squeezes the rest of the molecule together.

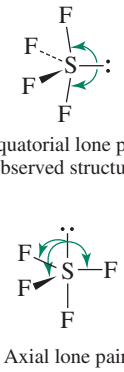


FIGURE 11 Possible Structures of SF_4.

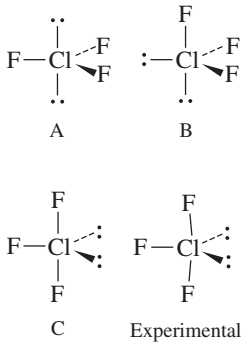


FIGURE 12 Possible Structures of ClF_3.

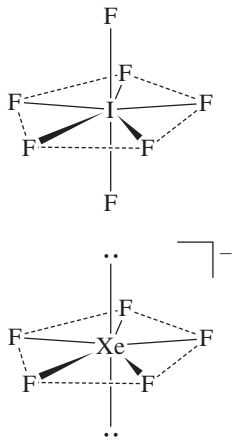
ClF_3 provides a second example of the influence of lone pairs in molecules having a steric number of 5. There are three possible structures for ClF_3, as shown in **Figure 12**.

In determining the feasibility of different structures, lone pair–lone pair interactions should be considered first, followed by lone pair–bonding pair interactions. These interactions at angles of 90° or less are generally considered destabilizing; larger angles generally render structures more feasible. For example, in ClF_3, structure B can be eliminated quickly because of the 90° *lp*−*lp* angle. The *lp*−*lp* angles are large for A and C, so the choice must come from the *lp*−*bp* and *bp*−*bp* angles. Because the *lp*−*bp* angles are more important, C, which has only four 90° *lp*−*bp* interactions, is favored over A, which has six such interactions. Experiments have confirmed that the structure is based on C, with slight distortions due to the lone pairs. The lone pair–bonding pair repulsion causes the *lp*–*bp* angles to be larger than 90° and the *bp*−*bp* angles to be less than 90° (actually, 87.5°). The Cl—F bond distances show the repulsive effects as well, with the axial fluorines (approximately 90° *lp*−*bp* angles) at 169.8 pm and the equatorial fluorine (in the plane with two lone pairs) at 159.8 pm.[8] Angles involving lone pairs cannot be determined experimentally.

Interaction	Angles in Possible Structures A	B	C	Experimental
lp–*lp*	180°	90°	120°	Cannot be determined
lp–*bp*	6 at 90°	3 at 90°	4 at 90°	Cannot be determined
		2 at 120°	2 at 120°	
bp–*bp*	3 at 120°	2 at 90°	2 at 90°	2 at 87.5°
		1 at 120°		Axial Cl—F 169.8 pm Equatorial Cl—F 159.8 pm

Additional examples of structures with lone pairs are illustrated in **Figure 13**. The structures based on a trigonal bipyramidal arrangement of electron pairs around a central atom always place any lone pairs in the equatorial plane, as in SF_4, BrF_3, and XeF_2. The resulting shapes minimize both lone pair–lone pair and lone pair–bonding pair repulsions. The shapes are called *seesaw* (SF_4), *distorted T* (BrF_3), and *linear* (XeF_2).

Steric Numbers = 6 and 7



In octahedral structures, all six positions are equivalent. When a single lone pair is present, it typically repels adjacent bonding pairs, reducing bond angles accordingly, as for IF_5 in Figure 13. In octahedron-based structures with two lone pairs, lone pair–lone pair repulsion is minimized if these pairs are *trans*, and this is the shape that is adopted. Square planar XeF_4, also shown in Figure 13, is an example. Recently XeF_3^-, which would be expected to have a steric number of 6 and three lone pairs, has been reported in the gas phase, but attempts to prepare salts of this ion have been unsuccessful.[9]

The shape that minimizes electron-pair repulsions for a steric number of 7 is the pentagonal bipyramid, shown in Figure 8. IF_7 (in the margin) and TeF_7^{2-} exhibit this shape, with both axial and equatorial fluorines. If a single lone pair is present, in some cases the lone pair causes distortion. The nature of this distortion is not always easy to ascertain; XeF_6 is a classic example.[10] In other cases the structure is octahedral (see Problem 26) with the lone pair not stereochemically active.* Two lone pairs minimize their repulsions by adopting axial (*trans*) positions, with the atoms all in the equatorial plane. Two known examples are XeF_5^- (in the margin) and IF_5^{2-}.

*A lone pair that appears in the Lewis-dot structure but has no apparent effect on the molecular geometry is classified as not stereochemically active. The VSEPR model assumes that all lone pairs are stereochemically active and therefore do affect the molecular geometry.

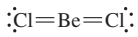
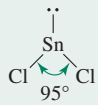
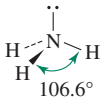
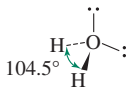
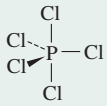
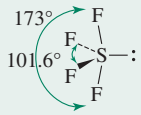
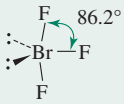
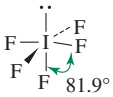
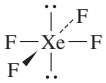
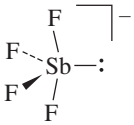
Steric Number	None	Number of Lone Pairs on Central Atom: 1	2	3
2				
3				
4				
5				
6				

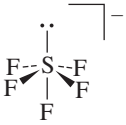
FIGURE 13 Structures Containing Lone Pairs.

EXAMPLE 4

SbF_4^- has a single lone pair on Sb. Its structure is therefore similar to SF_4, with a lone pair occupying an equatorial position. This lone pair causes considerable distortion, giving an F—Sb—F (axial positions) angle of 155° and an F—Sb—F (equatorial) angle of 90°.



SF_5^- has a single lone pair. Its structure is based on an octahedron, with the ion distorted away from the lone pair, as in IF_5.



SeF_3^+ has a single lone pair. This lone pair reduces the Se—F bond angle significantly, to 94°.

EXERCISE 2 Predict the structures of the following ions. Include a description of distortions from the ideal angles (for example, less than 109.5° because…).

NH_2^- NH_4^+ I_3^- PCl_6^-

2.2 Multiple Bonds

The VSEPR model considers double and triple bonds to have slightly greater repulsive effects than single bonds because of the repulsive effect of π electrons that increase the electron density between the bonded atoms beyond that present in a σ bond. For example, the $H_3C—C—CH_3$ angle in $(CH_3)_2C{=}CH_2$ is smaller, and the $H_3C—C{=}CH_2$ angle is larger than the trigonal 120° (**Figure 14**).[11]

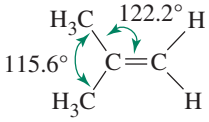
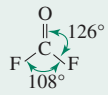
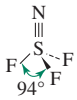
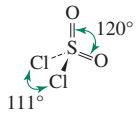
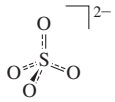
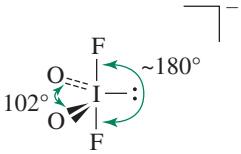


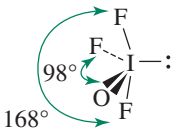
FIGURE 14 Bond Angles in $(CH_3)_2C{=}CH_2$.

Steric Number	Number of Bonds with Multiple Bond Character: 1	2	3	4
2		O=C=O		
3				
4				
5				
6				

* The bond angles of these molecules have not been determined accurately. However, spectroscopic measurements are consistent with the structures shown.

FIGURE 15 Structures Containing Multiple Bonds.





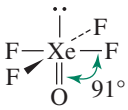


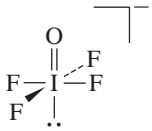
FIGURE 16 Structures Containing Both Lone Pairs and Multiple Bonds.

Additional examples of the effect of multiple bonds on molecular geometry are shown in **Figure 15**. Comparing Figures 13 and 15, we see that multiple bonds tend to occupy the same positions as lone pairs. For example, the double bonds to oxygen in SOF_4, ClO_2F_3, and XeO_3F_2 are all equatorial, as are the lone pairs in the matching compounds of steric number 5, SF_4, BrF_3, and XeF_2. Multiple bonds, like lone pairs, also tend to occupy more space than single bonds, causing distortions that squeeze the rest of the molecule together. In molecules that have both lone pairs and multiple bonds, these features may compete for space; examples are shown in **Figure 16**. As a generalization, lone pairs often have a greater influence than multiple bonds in dictating molecular geometry.

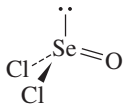
EXAMPLE 5

HCP, like HCN, is linear, with a triple bond: H—C≡P:

IOF_4^- has a single lone pair on the side opposite the oxygen. The lone pair has a slightly greater repulsive effect than the double bond to oxygen, as shown by the average O—I—F angle of 89°. (The extra repulsive character of the I=O bond places it opposite the lone pair.)



$SeOCl_2$ has both a lone pair and a selenium–oxygen double bond. The lone pair has a greater effect than the double bond; the Cl—Se—Cl angle is reduced to 97° by this effect, and the Cl—Se—O angle is 106°.



EXERCISE 3 Predict the structures of the following. Indicate the direction of distortions from the regular structures.

$XeOF_2$ $ClOF_3$ $SOCl_2$

2.3 Electronegativity and Atomic Size Effects

Electronegativity is a measure of an atom's ability to attract electrons from a neighboring atom to which it is bonded; it can be viewed as the ability of an atom to win the competition to attract shared electrons. Electronegativity was mentioned earlier as a guide in the use of formal charges. It also can play an important role in determining the arrangement of outer atoms around a central atom and in rationalizing bond angles. The effects of electronegativity and atomic size frequently parallel each other, but in some cases, the sizes of outer atoms and groups may play the more important role.

Electronegativity Scales

Linus Pauling introduced the concept of electronegativity in the 1930s as a means of describing bond energies. Pauling recognized that polar bonds have higher bond energies than nonpolar bonds formed from the same elements. For example, he observed that the bond energy of HCl, 432 kJ/mol, was much higher than the average of the bond energies of H_2 (436 kJ/mol) and Cl_2 (243 kJ/mol).* He related the difference between actual and average bond energies to the difference in electronegativity between the elements involved. He also made adjustments for the sake of convenience, most notably to give the elements C through F equally spaced values of 2.5 through 4.0.** Some early Pauling electronegativity values are in **Table 3**. The value of 4.0 for fluorine is still commonly used as a reference point for other electronegativity scales.

More recent values have been derived from other molecular and atomic properties, such as ionization energies and electron affinities. **Table 4** summarizes approaches used for a variety of electronegativity scales; examining differences among these is beyond the scope of this text. In most cases the different methods give similar electronegativity values, sometimes with the exception of the transition metals.[12] We choose to use the values reported by Mann, Meek, and Allen (**Table 5**) based on configuration energies (CE), the average ionization energies of valence electrons in ground state free atoms. For *s*- and *p*-block elements the configuration energies are defined as follows:[13]

$$\mathrm{CE} = \frac{n\varepsilon_s + m\varepsilon_p}{n + m}$$

where n = number of s electrons
m = number of p electrons
ε_s, ε_s = experimental 1-electron s and p energies†

TABLE 3 Early Values of Pauling Electronegativities

H 2.1			
C 2.5	N 3.0	O 3.5	F 4.0
Si 1.8	P 2.1	S 2.5	Cl 3.0
Ge 1.8	As 2.0	Se 2.4	Br 2.8

*Values used by Pauling, converted to kJ/mol. L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., 1960, Cornell University Press, Ithaca, NY, p. 81.

Earlier, Pauling had assigned fluorine an electronegativity of 2.00; see L. Pauling, *J. Am. Chem. Soc.*, **1932, *54*, 3570.

†Multiplet averaged values from C. E. Moore, *Ionization Potentials and Ionization Limits Derived From the Analyses of Optical Spectra*, NSRDS-NBS-34, Washington, D.C., 1971; *Atomic Energy Levels*, NSRDS-35, Washington, D.C., 1971, Vol. III.

TABLE 4 Electronegativity Scales

Principal Authors	Method of Calculation or Description
Pauling[14]	Bond energies
Mulliken[15]	Average of electron affinity and ionization energy
Allred & Rochow[16]	Electrostatic attraction proportional to Z^*/r^2
Sanderson[17]	Electron densities of atoms
Pearson[18]	Average of electron affinity and ionization energy
Allen[19]	Average energy of valence shell electrons, configuration energies
Jaffé[20]	Orbital electronegativities

TABLE 5 Electronegativity (Pauling Units)

1	2	12	13	14	15	16	17	18
H 2.300								He 4.160
Li 0.912	Be 1.576		B 2.051	C 2.544	N 3.066	O 3.610	F 4.193	Ne 4.787
Na 0.869	Mg 1.293		Al 1.613	Si 1.916	P 2.253	S 2.589	Cl 2.869	Ar 3.242
K 0.734	Ca 1.034	Zn 1.588	Ga 1.756	Ge 1.994	As 2.211	Se 2.424	Br 2.685	Kr 2.966
Rb 0.706	Sr 0.963	Cd 1.521	In 1.656	Sn 1.824	Sb 1.984	Te 2.158	I 2.359	Xe 2.582
Cs 0.659	Ba 0.881	Hg 1.765	Tl 1.789	Pb 1.854	Bi (2.01)	Po (2.19)	At (2.39)	Rn (2.60)

Source: J. B. Mann, T. L. Meek, L. C. Allen, *J. Am. Chem. Soc.*, **2000**, 122, 2780, Table 2.

The configuration energies are multiplied by a constant to give values comparable to the Pauling scale to enable convenient comparison between the scales.

Pauling's calculation of electronegativities from bond energies requires averaging over a number of compounds in an attempt to minimize experimental uncertainties and other minor effects. Methods that use ionization energies and other atomic properties can be calculated more directly. The electronegativities reported are suitable for most uses, but the actual values for atoms in different molecules can differ depending on the specific electronic environment of the atoms. The concept of electronegativity varying for a given atom on the basis of its specific bonds within a molecule is usually not introduced in introductory chemistry, but is a consequence of modern electronegativity scales.

It is important to emphasize that all electronegativities are measures of an atom's ability to attract electrons from a neighboring atom *to which it is bonded*. A critique of all electronegativity scales, and particularly Pauling's, is that each scale cannot be successfully applied to all situations; all of these scales have deficiencies on the basis of the specific assumptions used in their development.[21]

[*]For a recent approach that addresses some of the limitations of the Allen method, see P. Politzer, Z. P. Shields, F. A. Bulat, J. S. Murray, *J. Chem. Theory Comput.*, **2011**, *7*, 377.

With the exception of helium and neon, which have large calculated electronegativities and no known stable compounds, fluorine has the largest value, and electronegativity decreases toward the lower left corner of the periodic table. Although usually classified with Group 1 (IA), hydrogen is quite dissimilar from the alkali metals in its electronegativity, as well as in many other chemical and physical properties. Hydrogen's chemistry is distinctive from all the groups.

Electronegativities of the noble gases can be calculated more easily from ionization energies than from bond energies. Because the noble gases have higher ionization energies than the halogens, calculations suggest that the electronegativities of the noble gases may exceed those of the halogens (Table 5).[22] The noble gas atoms are somewhat smaller than the neighboring halogen atoms—for example, Ne is smaller than F—as a consequence of a greater effective nuclear charge. This charge, which is able to attract noble gas electrons strongly toward the nucleus, is also likely to exert a strong attraction on electrons of neighboring atoms; hence, the high electronegativities predicted for the noble gases are reasonable.

Electronegativity and Bond Angles

By the VSEPR approach, trends in many bond angles can be explained by electronegativity. Consider the bond angles in the following molecules:

Molecule	X–P–X Angle (°)	Molecule	X–S–X Angle (°)
PF_3	97.8	OSF_2	92.3
PCl_3	100.3	$OSCl_2$	96.2
PBr_3	101.0	$OSBr_2$	98.2

As the electronegativity of the halogen increases, the halogen exerts a stronger pull on electron pairs it shares with the central atom. This effect reduces the concentration of electrons near the central atom, decreasing somewhat the repulsion between the bonding pairs near the central atom, and allows the lone pair to have more impact in compressing the halogen–central atom–halogen angles. Consequently, the molecules with the most electronegative *outer* atoms, PF_3 and OSF_2, have the smallest angles.

If the central atom remains the same, molecules that have a larger difference in electronegativity values between their central and outer atoms have smaller bond angles. The atom with larger electronegativity draws the shared electrons toward itself and away from the central atom, reducing the repulsive effect of these electrons. The compounds of the halogens in **Table 6** show this effect; the compounds containing fluorine have smaller angles than those containing chlorine, which in turn have smaller angles than those containing bromine. The lone pair exerts a relatively larger effect, and forces smaller bond angles, as the electronegativity of the outer atom increases. An alternative explanation for this trend is size: as the size of the outer atom increases in the order F $<$ Cl $<$ Br, the bond angle increases. Additional compounds showing the effects of electronegativity on bond angles are also given in Table 6.

Similar considerations can be made in situations where the outer atoms remain the same, but the central atom is changed, for example,

Molecule	Bond Angle (°)	Molecule	Bond Angle (°)
H_2O	104.5	NCl_3	106.8
H_2S	92.1	PCl_3	100.3
H_2Se	90.6	$AsCl_3$	98.9

In these cases, as the central atom becomes more electronegative, it pulls electrons in bonding pairs more strongly toward itself, increasing the concentration of electrons near the central atom.

TABLE 6 Bond Angles and Lengths

Molecule	Bond Angle (°)	Bond Length (pm)	Molecule	Bond Angle (°)	Bond Length (pm)	Molecule	Bond Angle (°)	Bond Length (pm)	Molecule	Bond Angle (°)	Bond Length (pm)
H_2O	104.5	97	OF_2	103.3	96	OCl_2	110.9	170			
H_2S	92.1	135	SF_2	98.0	159	SCl_2	102.7	201			
H_2Se	90.6	146				$SeCl_2$	99.6	216			
H_2Te	90.2	169				$TeCl_2$	97.0	233			
NH_3	106.6	101.5	NF_3	102.2	137	NCl_3	106.8	175			
PH_3	93.2	142	PF_3	97.8	157	PCl_3	100.3	204	PBr_3	101.0	220
AsH_3	92.1	151.9	AsF_3	95.8	170.6	$AsCl_3$	98.9	217	$AsBr_3$	99.8	236
SbH_3	91.6	170.7	SbF_3	87.3	192	$SbCl_3$	97.2	233	$SbBr_3$	98.2	249

Source: N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford, 1997, pp. 557, 767; A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, Oxford, 1987, pp. 705, 793, 846, and 879; R. J. Gillespie and I. Hargittai, *The VSEPR Model of Molecular Geometry*, Allyn and Bacon, Needham Heights, MA, 1991.

The net effect is that an increase in bonding pair–bonding pair repulsions near the *central* atom increases the bond angles. In these situations the molecule with the most electronegative central atom has the largest bond angles. Additional examples can be found in Table 6, where molecules having the same outer atoms, but different central atoms, are shown in the same column.

EXERCISE 4

Which molecule has the smallest bond angle in each series?

a. $OSeF_2$ $OSeCl_2$ $OSeBr_2$ (halogen–Se–halogen angle)
b. $SbCl_3$ $SbBr_3$ SbI_3
c. PI_3 AsI_3 SbI_3

Effects of Size

In the examples considered so far, the most electronegative atoms have also been the smallest. For example, the smallest halogen, fluorine, is also the most electronegative. Consequently, we could have predicted the trends in bond angles on the basis of atomic size, with the smallest atoms capable of being crowded together most closely. It is important to also consider situations in which size and electronegativity might have opposite effects, where a smaller outer group is *less* electronegative than a larger group attached to a central atom. For example,

Molecule	C—N—C Angle (°)
$N(CH_3)_3$	110.9
$N(CF_3)_3$	117.9

In this case VSEPR would predict that the more electronegative CF_3 groups would lead to a smaller bond angle because they would withdraw electrons more strongly than CH_3 groups. That the bond angle in $N(CF_3)_3$ is actually 7° larger than in $N(CH_3)_3$ suggests that in this case, size is the more important factor, with the larger CF_3 groups requiring more space. The point at which the size of outer atoms and groups becomes more important

than electronegativity can be difficult to predict, but the potential of large outer atoms and groups to affect molecular shape should not be dismissed.

Molecules Having Steric Number = 5

For main group atoms having a steric number of 5, it is instructive to consider the relative bond lengths for axial and equatorial positions. For example, in PCl_5, SF_4, and ClF_3, the central atom–axial distances are longer than the distances to equatorial atoms, as shown in **Figure 17**. This effect has been attributed to the greater repulsion of lone and bonding pairs with atoms in axial positions (three 90° interactions) than with atoms in equatorial positions (two 90° interactions).

In addition, there is a tendency for less electronegative groups to occupy equatorial positions, similar to lone pairs and multiply bonded atoms. For example, in phosphorus compounds having both fluorine and chlorine atoms, in each case the chlorines occupy equatorial positions (**Figure 18**). The same tendency is shown in compounds having formulas PF_4CH_3, $PF_3(CH_3)_2$, and $PF_2(CH_3)_3$, with the less electronegative CH_3 groups also equatorial (**Figure 19**). One can envision the electron density of the P—A bond, where A is the less electronegative atom, being concentrated closer to the phosphorus in such cases, leading to a preference for equatorial positions by similar reasoning applied to lone pairs and multiple bonds.

The relative effects on bond angles by less electronegative atoms are, however, typically less than for lone pairs and multiple bonds. For example, the bond angle to equatorial positions opposite the Cl atom in PF_4Cl is only slightly less than 120°, in contrast to the greater reduction in comparable angles in SF_4 and SOF_4 (**Figure 20**).

Predicting structures in some cases is challenging. Phosphorus compounds containing both fluorine atoms and CF_3 groups provide an intriguing example. CF_3 is an electron withdrawing group whose electronegativity has been calculated to be comparable to the more electronegative halogen atoms.* Does CF_3 favor equatorial positions more strongly than F? Trigonal bipyramidal phosphorus compounds containing varying numbers of F and CF_3 groups with both axial and equatorial CF_3 groups are known (**Figure 21**). When two or three CF_3 groups are present, the orientations are truly a challenge to explain: these groups are axial in $PF_3(CF_3)_2$ but equatorial in $PF_2(CF_3)_3$! In both cases the more symmetrical structure, with identical equatorial groups, is preferred.**

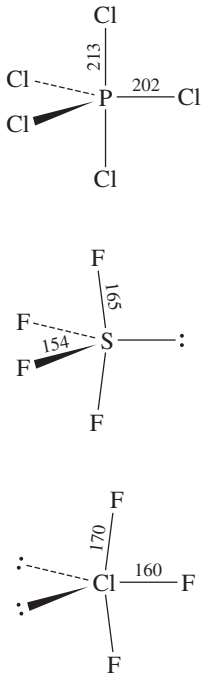


FIGURE 17 Bond Distances in PCl_5, SF_4, and ClF_3.

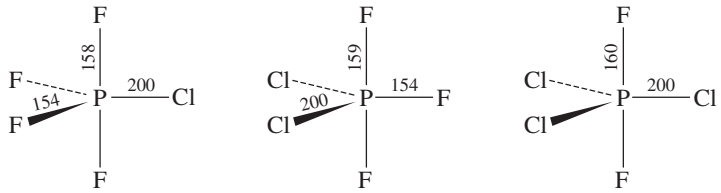


FIGURE 18 $PClF_4$, PCl_2F_3, and PCl_3F_2.

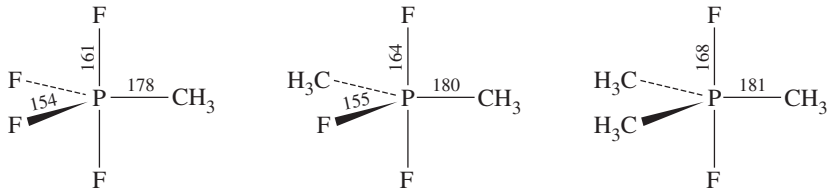


FIGURE 19 PF_4CH_3, $PF_3(CH_3)_2$, and $PF_2(CH_3)_3$.

*For an analysis of different approaches to determining the electronegativity of CF_3, see J. E. True, T. D. Thomas, R. W. Winter, G. L. Gard, *Inorg. Chem.*, **2003**, *42*, 4437.

See H. Oberhammer, J. Grobe, D. Le Van, *Inorg. Chem.*, **1982, *21*, 275 for a discussion of these structures.