

1

Atomic Structure & Chemical Bonding

Goal To understand why atoms form molecules.

Objectives

After this chapter, you should be able to

- interpret the properties of elements that are important for life from the periodic table.
- understand why and how atoms form bonds.
- draw Lewis dot and line structures to represent chemical bonds.

What is life? Why is an elephant alive but a table inert? Why are cells alive but their contents when transferred to a flask inanimate? The answers to questions about the nature of life lie in the chemistry of the atoms and molecules that make up living things. Life is an emergent property of the structure and reactivity of atoms and their capacity to make and break bonds with each other. Understanding the basis for life is inseparable from understanding the principles that govern the behavior of atoms and molecules. In the chapters that follow, we will focus on the concepts of chemistry that are necessary for understanding life and apply these concepts to understanding how living things work. We begin with an explanation of why and how atoms bond together to form molecules.

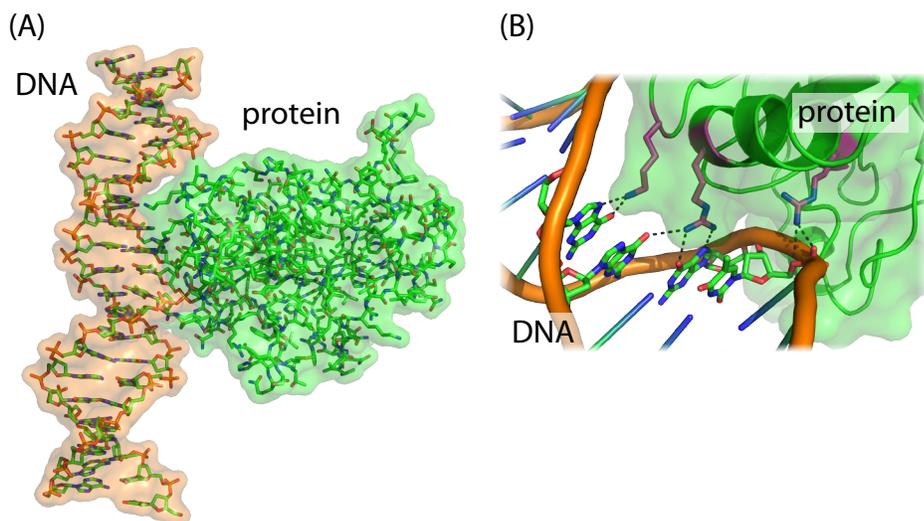
Life is based on chemical interactions

Let us start with an example of why understanding the properties of atoms and molecules is essential for understanding living systems. Figure 1A shows a protein, depicted in green, attached to a DNA molecule, shown in orange. The association between this specific protein, called p53, and DNA is essential for maintaining the integrity of the human genome. Without this interaction, cells mutate rapidly and cancer develops. In fact, p53 is so important that its malfunction is implicated in about half of all human cancers.

To understand how p53 is able to interact with DNA, it is important to recognize that both proteins and DNA are composed of many thousands of atoms (shown as connected by lines in Figure 1A). These large molecules,

Figure 1 Fundamental properties of living systems emerge from atomic-level structural and chemical features

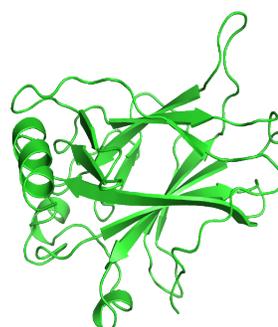
(A) A protein (*green*) interacts with DNA (*orange*). (B) The interaction is mediated by attractive forces between specific atoms in the protein and specific atoms in the DNA, as indicated with black dotted lines.



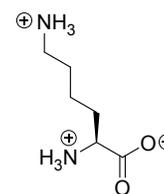
or **macromolecules**, interact with one another because particular atoms in one molecule are attracted to particular atoms in the other molecule. Figure 1B highlights a few of the key attractions that exist between atoms in p53 and DNA (shown as black dotted lines). The alteration of just one or two specific atoms would dramatically reduce the ability of p53 to bind to DNA. We will examine the nature of these interactions later, but for now it is important to appreciate that the identities and chemical properties of just a handful of atoms within a molecule consisting of thousands of atoms can be critical for the functioning of living systems. As you will see, many properties associated with life emerge from the structures of molecules and the ways in which they interact with one another. To understand how molecules interact, we first need to learn more about the atoms and bonds of which they are composed. In Chapter 2, we will examine the attractive forces that cause atoms in different molecules to interact with one another.

Figure 2 Many important molecules of life are macromolecules

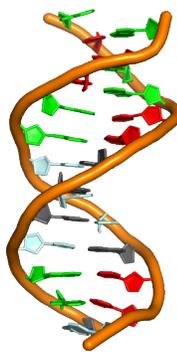
Shown are the three-dimensional structures of two macromolecules, a protein and DNA. A representative monomer subunit for each macromolecule is shown to the right.



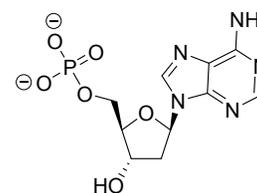
Protein



Amino acid



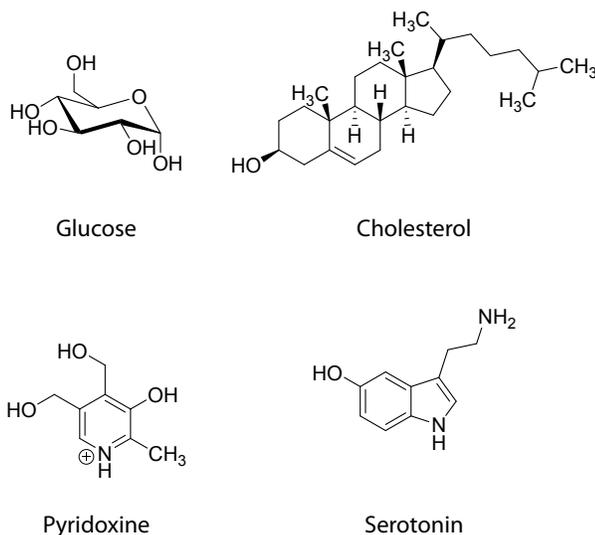
DNA



Nucleotide

Figure 3 Myriad small molecules are important for life

Shown are examples that illustrate the diverse roles that small molecules play in living systems. Glucose is a sugar that is used as an energy source; cholesterol is a component of animal cell membranes; pyridoxine is a vitamin (B_6); and serotonin is a neurotransmitter.



Cells consist of macromolecules and small molecules

Proteins and DNA are polymers of amino acids and nucleotides, respectively (Figure 2). These and other kinds of macromolecules carry out the biological processes that make life possible. For example, some macromolecules store genetic information that is passed down to future generations. Some are involved in decoding genetic information. Yet other macromolecules carry out metabolism, breaking down molecules to obtain energy and using that energy to build other molecules.

In addition to macromolecules, **small molecules** play a central role in living systems. Although there is no discrete size cut-off that distinguishes “small” molecules from macromolecules, most small molecules that are relevant to life contain fewer than about a hundred atoms. Unlike macromolecules, which are polymers of repeating units, small molecules are diverse in their structures and typically lack repeating units. Their diversity implies that small molecules are synthesized in the cell by a more diverse collection of chemical reactions than those used to make macromolecules. Indeed, as we will learn later, macromolecules are typically generated by repeating one type of chemical reaction over and over, while small molecules are synthesized through the use of thousands of different reactions. Figure 3 shows examples of small molecules that occupy center stage in the story of life. Here, we are concerned with the chemical rules that govern how the atoms in these molecules interact with each other.

It is important to remember that in a cell these macromolecules and small molecules are bathed in water along with an enormous number of ions (salts). As we shall see, water affects the way that all other molecules in the cell function; indeed, life itself could not exist without an aqueous environment.

The periodic table arranges atoms according to numbers of protons, numbers of electron shells, and valence electrons

Molecules are composed of **atoms**, which are the units of matter that correspond to the elements in the periodic table of elements (Figure 4). Only a few elements are abundant in cells. In fact, the vast majority of

	I																	VIIIA			
1	Hydrogen 1 H	IIA										IIIA					IVA	VA	VIA	VIIA	Helium 2 He
2	Lithium 3 Li	Beryllium 4 Be											Boron 5 B	Carbon 6 C	Nitrogen 7 N	Oxygen 8 O	Fluorine 9 F	Neon 10 Ne			
3	Sodium 11 Na	Magnesium 12 Mg	IIIB	IVB	VB	VIB	VII B	VIII B				IB	IIB	Aluminum 13 Al	Silicon 14 Si	Phosphorus 15 P	Sulfur 16 S	Chlorine 17 Cl	Argon 18 Ar		
4	Potassium 19 K	Calcium 20 Ca	Scandium 21 Sc	Titanium 22 Ti	Vanadium 23 V	Chromium 24 Cr	Manganese 25 Mn	Iron 26 Fe	Cobalt 27 Co	Nickel 28 Ni	Copper 29 Cu	Zinc 30 Zn	Gallium 31 Ga	Germanium 32 Ge	Arsenic 33 As	Selenium 34 Se	Bromine 35 Br	Krypton 36 Kr			
5	Rubidium 37 Rb	Strontium 38 Sr	Yttrium 39 Y	Zirconium 40 Zr	Niobium 41 Nb	Molybdenum 42 Mo	Technetium 43 Tc	Ruthenium 44 Ru	Rhodium 45 Rh	Palladium 46 Pd	Silver 47 Ag	Cadmium 48 Cd	Indium 49 In	Tin 50 Sn	Antimony 51 Sb	Tellurium 52 Te	Iodine 53 I	Xenon 54 Xe			
6	Cesium 55 Cs	Barium 56 Ba	Lutetium 71 Lu	Hafnium 72 Hf	Tantalum 73 Ta	Tungsten 74 W	Rhenium 75 Re	Osmium 76 Os	Iridium 77 Ir	Platinum 78 Pt	Gold 79 Au	Mercury 80 Hg	Thallium 81 Tl	Lead 82 Pb	Bismuth 83 Bi	Polonium 84 Po	Astatine 85 At	Radon 86 Rn			
7	Francium 87 Fr	Radium 88 Ra	Lawrencium 103 Lr	Rutherfordium 104 Rf	Dubnium 105 Db	Seaborgium 106 Sg	Bohrium 107 Bh	Hassium 108 Hs	Meitnerium 109 Mt	Darmstadtium 110 Ds	Roentgenium 111 Rg	Ununbium 112 Uub	Ununtrium 113 Uut	Ununquadium 114 Uuq	Ununpentium 115 Uup	Ununhexium 116 Uuh	Ununseptium 117 Uus	Ununoctium 118 Uuo			
	Lanthanides	Lanthanum 57 La	Cerium 58 Ce	Praseodymium 59 Pr	Neodymium 60 Nd	Promethium 61 Pm	Samarium 62 Sm	Europium 63 Eu	Gadolinium 64 Gd	Terbium 65 Tb	Dysprosium 66 Dy	Holmium 67 Ho	Erbium 68 Er	Thulium 69 Tm	Ytterbium 70 Yb						
	Actinides	Actinium 89 Ac	Thorium 90 Th	Protactinium 91 Pa	Uranium 92 U	Neptunium 93 Np	Plutonium 94 Pu	Americium 95 Am	Curium 96 Cm	Berkelium 97 Bk	Californium 98 Cf	Einsteinium 99 Es	Fermium 100 Fm	Mendelevium 101 Md	Nobelium 102 No						

Figure 4 Most living matter is composed of just six elements in the periodic table

Hydrogen, carbon, nitrogen, oxygen, phosphorus, and sulfur, highlighted in yellow, make up nearly all living matter.

biological matter, about 99%, is made of just six elements: carbon, hydrogen, nitrogen, oxygen, sulfur, and phosphorus. Most biological molecules, such as proteins, carbohydrates, lipids, and nucleic acids, are *exclusively* composed of these elements. A few other atoms also play roles in biology; these include calcium, chlorine, iron, magnesium, potassium, sodium, and zinc. Most of the many elements in the periodic table are not necessary for life.

Atoms, in turn, are composed of particles known as **protons**, **neutrons**, and **electrons**. Protons and neutrons reside in the atomic nucleus and account for almost all of the mass of the atom. The number of protons present in an atom's nucleus, its **atomic number**, determines the identity of that atom as an element. The elements are numbered and arranged on the periodic table by their atomic numbers. Protons and electrons both possess electrical charges that are key determinants of atomic properties. Protons carry a positive charge that is balanced by the negative charge carried by electrons. While of a different polarity, or sign, the charge of a proton is precisely equal in magnitude to the charge of an electron; therefore, an atom with an equal number of protons and electrons will have an overall neutral charge. Neutrons have no charge and thus do not affect an atom's overall charge.

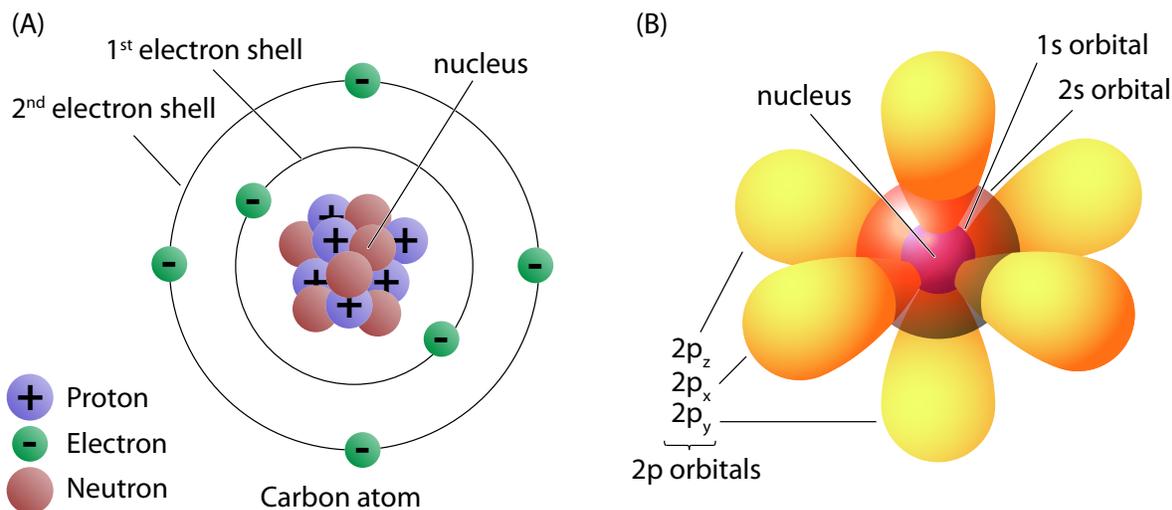


Figure 5 Electrons are organized into shells and orbitals

Shown is the electronic structure of a carbon atom. Carbon contains six protons, and a carbon atom that is neutrally charged contains six electrons, as shown. In (A), electrons are shown in electron shells. The first electron shell can hold only two electrons, and in the case of the carbon atom, this shell is filled. The second electron shell can hold up to eight electrons, but in carbon, it contains only four electrons. In (B) the electrons are shown in orbitals. The first electron shell contains only a single 1s orbital. The second electron shell contains four orbitals: a single 2s orbital and three 2p orbitals. The 2p orbitals are termed 2p_z, 2p_x, and 2p_y to signify that they are aligned along three orthogonal axes.

Electrons reside in shells and orbitals

The arrangement of electrons around the atomic nucleus is complex, and electrons do not simply orbit the nucleus as a planet would orbit a star. Broadly speaking, electrons are located in concentric **shells** that surround the nucleus. The shells that are closer to the nucleus are generally lower in energy than the shells that are farther from the nucleus, meaning that placing an electron in a shell that is closer to the nucleus is more stable and more favorable than placing an electron in a shell that is farther from the nucleus. Because of this, electrons fill shells from the inside to the outside; electrons in atoms with few electrons are in shells close to the nucleus, whereas atoms with many electrons first utilize the shells that are closer to the nucleus and then those that are farther from the nucleus once the inner shells are filled. The number of electrons that can occupy a shell increases with distance from the nucleus. The shell that is closest to the nucleus can contain only two electrons, whereas the second, third, and fourth electron shells can contain eight, 18, and 32 electrons, respectively.

Each shell, in turn, consists of **orbitals** that can each hold up to two electrons. Orbitals describe the probability of finding an electron in a given region of space (Figure 5). Orbitals are probabilistic descriptions, as the rapid movement of electrons makes their precise location at any given time uncertain. The physical space in which an electron is likely to be found is known as an **electron cloud**. Orbitals are classified based on their shape; for example, “s” orbitals are spheres that surround the nucleus, whereas “p” orbitals are dumbbell-shaped, with two lobes that lie on opposite sides of the nucleus. The first electron shell, which can only hold two electrons, contains a single s orbital. Because it is part of the innermost electron shell,

we refer to it as the “1s” orbital. The second electron shell can hold eight electrons, and as such, it contains four orbitals: a single s orbital and three p orbitals. These p orbitals are oriented orthogonally to one another, with each orbital lying parallel to one of the x, y, or z axes. The **electron configuration** of an atom describes how electrons in that atom are arranged into electron shells and orbitals. For example, carbon, which has six electrons when it is neutral, has an electron configuration of “ $1s^2 2s^2 2p^2$,” signifying that the carbon atom contains two electrons in its 1s orbital, two electrons in its 2s orbital, and two electrons in its 2p orbitals.

The periodic table arranges elements in order of increasing numbers of protons from left to right in a stacked series of rows (Figure 4). These rows are called **periods**. Elements in the same period share the same outermost shell but have different numbers of electrons. Thus, the outermost shell for carbon (C), nitrogen (N), and oxygen (O), which are all in the second period, is the second shell, with each element having different numbers of electrons in that shell. The electrons in the outermost shell are known as **valence** electrons. Thus, carbon, nitrogen and oxygen have 4, 5 and 6 valence electrons, respectively. Likewise, the outermost shell for elements in the third period is the third shell, and so on. Elements in the periodic table are also stacked on top of each other in columns called **groups**. Elements in the same group have the same number of valence electrons. For example, nitrogen and phosphorus (P), which are both in group VA, each contain five valence electrons. Valence electrons are involved in almost all chemical reactions and determine the bonds that atoms make.

Periods and groups in the periodic table reveal trends in the electronegativity of atoms

Electronegativity describes the tendency of an atom to gain or lose electrons and its tendency to attract electrons towards itself. Weakly electronegative atoms tend to give up electrons and form **cations** (positively charged atoms), whereas strongly electronegative atoms acquire electrons and become **anions** (negatively charged atoms). Electronegativity is a function of the **effective nuclear charge**, which is the amount of positive charge from the nucleus that a particular electron experiences. A large effective nuclear charge corresponds to a strong attraction between an electron and the nucleus. Effective nuclear charge increases as the charge of the nucleus increases. Consequently, electrons in atoms with more protons experience a greater effective nuclear charge than otherwise equivalent electrons in atoms with fewer protons.

The electronegativity of an element is revealed by its position in the periodic table. Electronegativity tends to increase from left to right within the periods of the periodic table, as the number of protons, and thus the effective nuclear charge, increases. However, the noble gases in group VIIIA are inert and do not have electronegativity values. Atoms in groups I and II (on the left) have less nuclear charge and are less electronegative than the corresponding atoms of the same period in group VII (on the right). Consequently, group I and II atoms tend to give up electrons to form cations, whereas atoms in group VII tend to acquire electrons to form anions.

Table of Electronegativity Values

	I							VIII		
1	H 2.1							He -		
2	Li 1.0	II	Be 1.5		III	IV	V	VI		
					B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne -
3	Na 0.9	Mg 1.2			Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar -

Figure 6 Electronegativity can be quantified

Several systems are used for quantifying the electronegativity of atoms. One of these, the Pauling system, is used in this book. Shown is an excerpt from the periodic table showing the Pauling electronegativity values for selected elements. Larger values indicate greater electronegativity. The noble gases (group VIII) are not assigned electronegativity values.

The effective nuclear charge decreases as the electron shell number increases, as outer-shell electrons are shielded from the positive charge of the nucleus by the inner-shell electrons that lie between them and the nucleus. Thus, the electronegativity within a group of elements decreases as the period number increases (moving from top to bottom). Because of these trends, the most electronegative elements are located at the top right of the periodic table, with fluorine (F) being the most electronegative (Figure 6). The concept of electronegativity is fundamental to understanding how atoms interact with each other to form the molecules of life, as we will now discuss.

Molecules are made of bonded atoms

Atoms connect with each other through **chemical bonds** to form molecules. Electronegativity strongly influences how atoms interact with each other and how they combine to form molecules. In fact, the electronegativity difference between two bonded atoms determines the nature of the chemical bond that forms between them. If the electronegativity difference is large, the bond that forms between the atoms will be an **ionic bond**, and if it is small, a **covalent bond** will generally form.

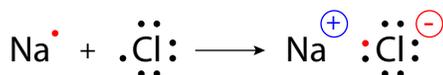


Figure 7 Sodium chloride contains ionic bonds

Sodium and chlorine form an ionic bond due to their large electronegativity difference. When a neutral sodium atom reacts with a neutral chlorine atom, it gives up its valence electron (depicted as a red dot; see Figure 9 for a further explanation of this atomic representation) to chlorine, resulting in oppositely charged Na^+ and Cl^- ions. An ionic bond results from the electrostatic attraction between these ions.

Ionic bonds form due to attraction between oppositely charged ions

An ionic bond is an electrostatic attraction between two adjacent, oppositely charged ions. Ionic bonds can exist in isolation or in vast networks that hold atoms together in crystalline solids. Ionic bonds can form when two ions come in contact with one another, or they can form when two uncharged atoms react with one another to form oppositely charged ions. In the latter scenario, the more-electronegative atom strips an electron from the less-electronegative atom, yielding an anion and a cation that are electrostatically attracted to one another. An example of such a reaction occurs when sodium and chlorine react to form sodium chloride (NaCl) (Figure 7). The chlorine atom is much more electronegative than the sodium atom; therefore, when they react, sodium gives up an electron to chlorine to

yield sodium (Na^+) and chloride (Cl^-) ions, which then form an ionic bond. Generally, an ionic bond is formed when the electronegativity difference between atoms is greater than 1.7. In the case of sodium chloride, sodium has an electronegativity of 0.9 and chlorine has an electronegativity of 3.0. The electronegativity difference between sodium and chlorine is 2.1, and since this difference is greater than 1.7, one would expect a bond between sodium and chlorine to be ionic. Many biological molecules, including the DNA and protein depicted in Figure 1, interact by forming ionic bonds; we will learn more about such bonds in the next chapter.

Covalent bonds form when electrons are shared between atoms

When two atoms form a bond and their electronegativity difference is smaller than 1.7, they tend to form covalent bonds in which electrons are shared between the two atoms. This is in contrast to ionic bonds, in which only one of the atoms assumes principal ownership of the electron. Most of the chemical bonds that make up the molecules of life are covalent bonds. As we will see in Chapter 2, some covalent bonds involve unequal sharing of electrons between atoms. Even in these so-called polar covalent bonds, the electronegativity difference is still less than 1.7.

In a single covalent bond, two valence electrons are shared by the two bonded atoms. For example, a water molecule is made of one oxygen atom connected to two hydrogen atoms through single covalent bonds. However, some covalent bonds involve the sharing of more than one pair of electrons between atoms. Double and triple bonds involve the sharing of four and six valence electrons, respectively. As an example, we will see below that nitrogen gas (N_2) involves the sharing of six valence electrons between its two nitrogen atoms.

The formation of bonds releases energy and the cleavage of bonds requires energy

Bonds form because favorable interactions between orbitals and the electrons in those orbitals allow the system to become more stable. As a result, the formation of a bond is accompanied by the release of energy, usually as heat. Conversely, when a bond breaks, it goes from a more-stable to a less-stable state, which requires an input of energy. The store of energy that is released during bond formation is also referred to as potential energy. The release of energy during bond formation results in a bond with lower potential energy. The formation of a strong (i.e., more-stable) bond results in the release of more energy than the formation of a weak bond.

The Lennard-Jones potential curve describes how the energy of a bond varies as a function of the distance between the nuclei of the bonded atoms (Figure 8). As the atoms move closer to one another, the attractive interactions between the two atoms become stronger until the distance between them is equal to the optimal bond distance. If the atoms move closer to one another than the optimal bond distance, the energy of the system increases abruptly due to the enormous repulsive forces that exist between the positively charged nuclei of the bonded atoms. We can quantify the strength of a

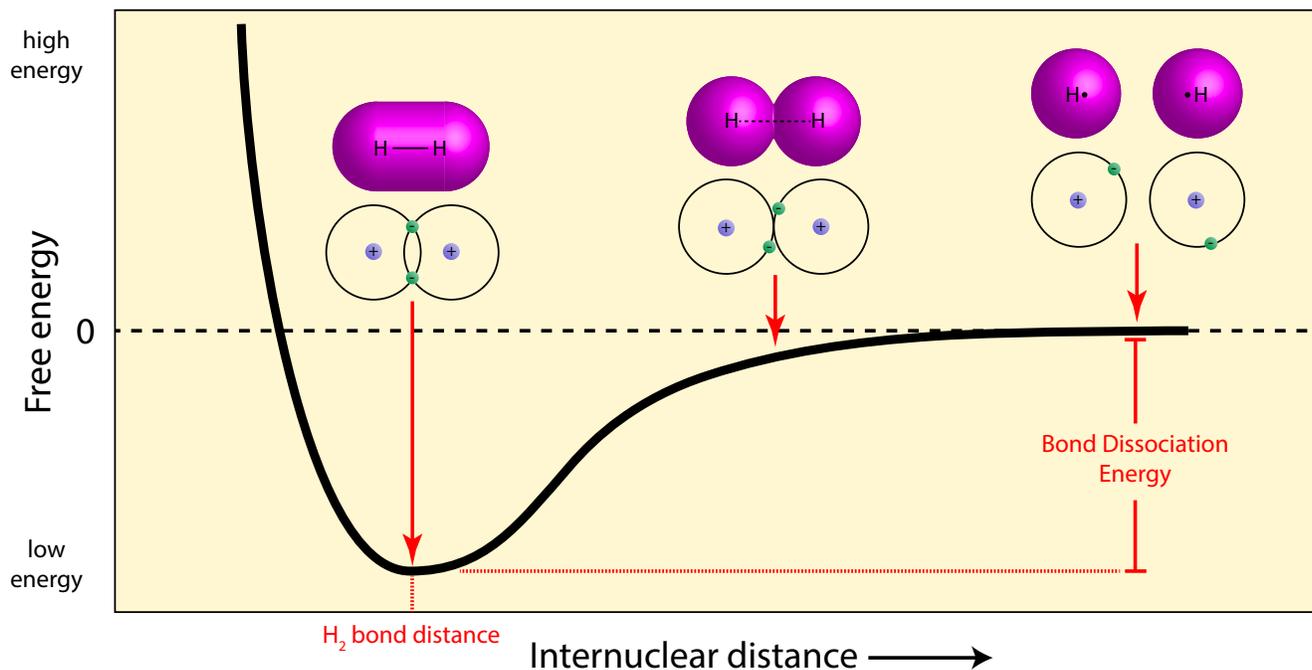


Figure 8 The Lennard-Jones curve describes the energy of a bond as a function of bond distance

The free energy of an H-H bond is plotted against the distance between the two nuclei. The distance between the nuclei in an H_2 molecule is 0.74 ångströms (Å; 1 Å is 0.1 nm). When the internuclear distance is small (less than 0.74 Å), the positive nuclei repel one another. Conversely, when the nuclei are far apart (greater than 0.74 Å), the s orbitals that contain the electrons cannot overlap, and no electron sharing can occur. Energy is minimized at an intermediate internuclear distance (0.74 Å) that equals the bond distance. At that point, the atomic orbitals overlap and electrons are shared, which releases energy. Similarly, the separation of two bonded atoms requires an input of energy equal to the bond dissociation energy (104 kcal/mol in the example shown).

chemical bond by measuring its **bond dissociation energy**, which is the amount of energy required to completely separate two bonded atoms. On the Lennard-Jones curve, the bond dissociation energy can be visualized as the difference in energy between the minimum point on the curve (where the internuclear distance equals the optimal bond distance) and the point at which the internuclear distance becomes infinitely large. The bond dissociation energy for a particular bond is dependent upon the molecule in which it is located; for example, the oxygen-hydrogen bond dissociation energy in a water molecule is slightly different from the oxygen-hydrogen bond dissociation energy in methanol (CH_3OH). The average of all known bond dissociation energy values for a particular covalent bond between two specific atoms is termed the bond energy. Bond energy values allow chemists to crudely compare the strengths of different types of covalent bonds. Generally speaking, most covalent bonds have bond energies of 80-100 kcal/mol.

Atoms tend to form bonds until their valence electron shell is filled

The atoms that make up the molecules of life—sulfur, phosphorus, oxygen, nitrogen, carbon, and hydrogen—form predictable numbers of bonds to other atoms. Generally speaking, each atom will form as many bonds as are necessary to completely fill its outermost electron shell. For example, oxygen is in group VI, and it has six valence electrons, but there is space

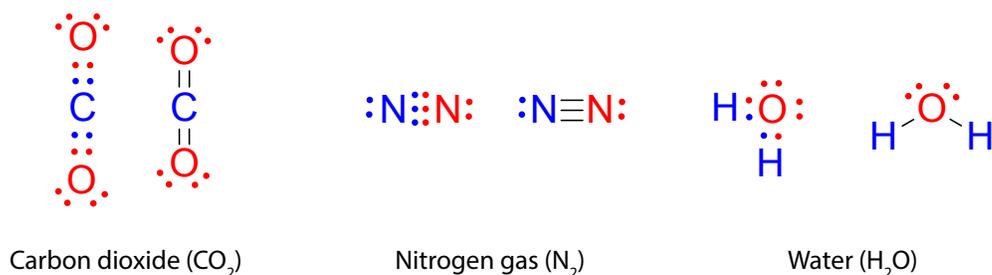


Figure 9 Covalent bonds can be represented with dots or lines

Covalent bonds are most commonly represented with dots or lines. Each dot represents one electron, with shared electrons drawn between two atoms and non-bonded electron pairs drawn adjacent to only the atom to which they belong. In contrast, each line represents two shared electrons. The number of electrons drawn between bonded atoms denotes the number of electrons being shared. Atoms and electrons are colored in the figure to indicate the atom from which the electrons were derived before bonds were formed. Only valence electrons are shown in Lewis structures; inner-shell electrons are assumed to be present but are not shown.

for eight electrons in its valence shell. Each hydrogen atom has one valence electron, but there is space for two electrons in its valence shell. When two hydrogen atoms and one oxygen atom come together to form water, oxygen shares one valence electron with each of the two hydrogen atoms to form two covalent bonds. Each hydrogen atom then has two valence electrons, completing their valence shells, and oxygen has eight valence electrons, completing its valence shell.

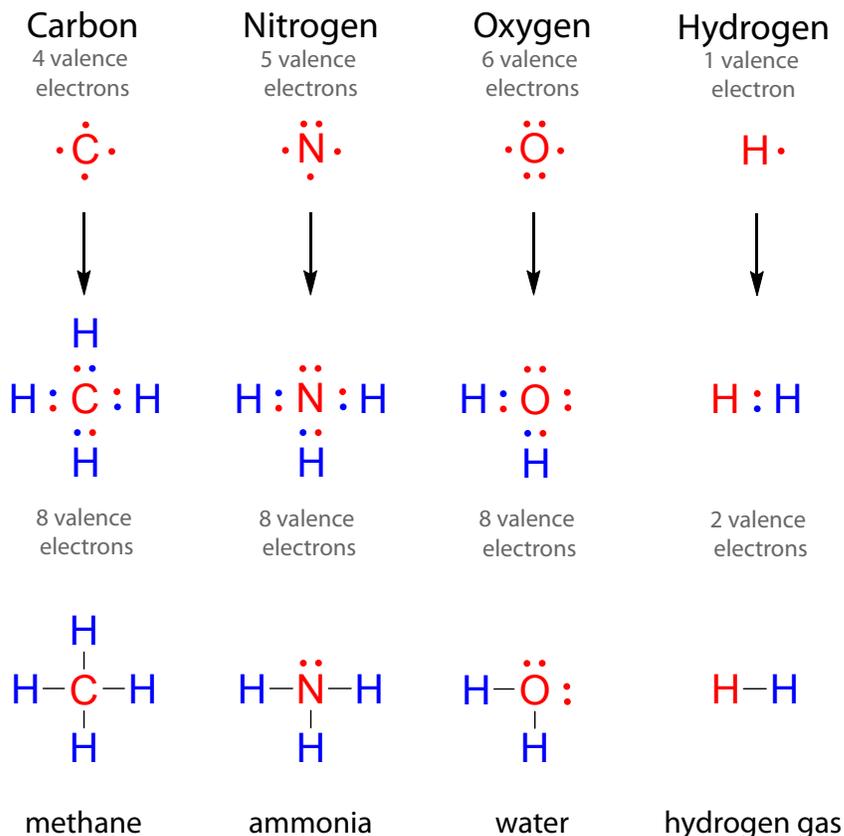
The sharing of valence electrons between atoms can be represented visually using a **Lewis “dot” structure** in which covalent bonds are represented by pairs of dots that represent the electrons shared between adjacent atoms. While these structures are a good way to visualize the locations of valence electrons, they can be time-consuming to draw. A simpler alternative is the **Lewis structure**, in which a single covalent bond is depicted by a single line connecting two atoms. Each line represents two electrons that are being shared between the connected atoms (Figure 9). We will represent bonds as lines, and restrict the use of dots to indicate non-bonded electrons.

Atoms can fill their outermost shells by forming single bonds with several different atoms or by forming double or triple bonds to the same atom. In a double bond, each atom shares two electrons with the other atom, for a total of four shared electrons. A double bond is represented by two parallel lines connecting adjacent atoms. By extension, a triple bond, in which six total valence electrons are shared, is represented by three parallel lines connecting adjacent atoms. Later in this chapter we will come to examples of carbon atoms forming single, double, and triple bonds.

Generally, the length of a chemical bond decreases as the number of bonds increases; therefore, double bonds are shorter than single bonds and triple bonds are shorter than double bonds. For example, a double bond between carbon and oxygen has a bond distance of about 1.22 ångströms (Å; 1 Å is 0.1 nm), which is substantially shorter than a C-O single bond (1.42 Å). Similarly, a triple bond between two nitrogen atoms has a bond distance of 1.10 Å, which is shorter than a nitrogen-nitrogen double bond (1.22 Å), which is shorter than a nitrogen-nitrogen single bond (1.45 Å). Bond strength, or the energy required to break a bond, tends to increase as bond length decreases. This is another way of saying that the potential energy of

Figure 10 Most elements form bonds in order to fill their valence electron shells

When atoms form covalent bonds, they tend to form a specific number of bonds such that they share enough electrons to fill their valence electron shells. Carbon, nitrogen, oxygen, and hydrogen all follow this trend. This figure shows the bonds that each of these elements would need to form with hydrogen to fill its valence shell. The resulting molecules are drawn using both the Lewis dot (*middle row*) and Lewis structure (*bottom row*) conventions.



bonds decreases (i.e., their stability increases) as bond length decreases.

The number of bonds that an atom will form can be predicted by the number of electrons that atom needs to fill its valence electron shell. Hydrogen, for example, requires two electrons to fill its outermost shell and therefore tends to form one single covalent bond to another atom. This arrangement gives hydrogen access to two electrons, allowing it to fill its valence shell. Meanwhile, atoms in the second and third periods (including carbon, nitrogen, oxygen, and sometimes sulfur and phosphorus) have a strong tendency to arrange their electrons such that a total of eight valence electrons are associated with every atom; this phenomenon is known as the **octet rule** (Figures 10 and 11). Carbon has four valence electrons but can accommodate eight electrons in its valence shell, and it therefore tends to

Figure 11 The elements found in life form a predictable number of bonds

Hydrogen, carbon, nitrogen, and oxygen have a predictable number of lone pairs and bonds when they are neutrally charged. Because of octet expansion, sulfur and phosphorus can form varying numbers of bonds and still remain neutral.

	Hydrogen	Carbon	Nitrogen	Oxygen	Phosphorus	Sulfur
Lewis dot structure of free atom	$\text{H}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\text{C}}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\text{N}}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\text{O}}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\text{P}}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\text{S}}}\cdot$
# of valence electrons	1	4	5	6	5	6
# of lone pairs	0	0	1	2	1 or 0	2, 1, or 0
# of bonds	1	4	3	2	3 or 5	2, 4, or 6

form four covalent bonds. When a carbon atom forms four single covalent bonds to four other atoms (as in methane, CH₄), it has engaged all of its valence electrons in covalent bonds while satisfying the octet rule and filling its valence electron shell. Nitrogen has five valence electrons, so it needs to form three covalent bonds to satisfy the octet rule. In this case, three of its five electrons are involved in covalent bonds (representing a total of six electrons), whereas the other two are represented as a **lone pair** (or non-bonded pair) belonging only to nitrogen. Oxygen, which has six valence electrons, must participate in two covalent bonds to complete its octet. This means that oxygen retains two pairs of non-bonded electrons that are not shared with any other atom. Non-bonded lone pairs of electrons are depicted in both Lewis structures and Lewis dot structures as a pair of dots drawn next to the atom to which they belong.

Phosphorus and sulfur, which are found in all living matter, are in period 3, and because the valence shell of elements in periods 3 and higher can hold more than eight electrons, these elements do not always follow the octet rule. Phosphorus and sulfur can use their “d” orbitals, in addition to their 3s and 3p orbitals, to form bonds, allowing them to possess more than eight valence electrons. Phosphorus can stably possess eight or 10 valence electrons, and sulfur can stably possess eight, 10, or 12 valence electrons. **Octet expansion** indicates that an atom’s valence shell contains more than eight electrons.

Box 1 Formal charge is a convention used to label charged atoms in molecules

Charges play a key role in determining how molecules react and interact with each other, and therefore formal charges are included in Lewis structures and most other molecular representations. **Formal charge** is a formalism that compares the number of electrons that an atom in a molecule possesses to the number of electrons in the free, neutral atom. If an atom in a molecule has the same number of valence electrons as the free, neutral atom, it has no formal charge. If it has more valence electrons than the neutral atom, it bears a negative formal charge; if it has fewer, it bears a positive formal charge. Formal charge is calculated for each atom using the general formula shown below:

$$\text{Formal Charge} = \begin{array}{l} \text{\# of valence} \\ \text{electrons in the} \\ \text{free, neutral atom} \end{array} - \begin{array}{l} \text{\# of "lone pair"} \\ \text{electrons} \end{array} - \frac{1}{2} \begin{array}{l} \text{\# of electrons} \\ \text{involved in bonds} \end{array}$$

The general formula for calculating formal charge works for atoms that obey the octet rule as well as atoms like sulfur and phosphorus that have expanded octets. The figure below shows the formal charges of some chemicals that are prevalent in biology.

	Hydrogen		Carbon	Oxygen			Nitrogen	
Bonds	0	1	4	1	2	3	3	4
Lone Pairs	0	0	0	3	2	1	1	0
Formal Charge	+1	0	0	-1	0	+1	0	+1
Example	H ⁺	H-H						

Box 2 Drawing Lewis dot structures

A valid Lewis dot structure shows all non-zero formal charges, satisfies the octet rule for each atom, and contains the correct number of atoms and valence electrons. A Lewis dot structure can be constructed from a molecular formula using the following steps:

1. Determine the total number of valence electrons that must appear in the structure by summing the valence electrons from all of the atoms. If the compound is charged, add an electron for each unit of negative charge and subtract an electron for each unit of positive charge.
2. Write the symbols for the atoms in a plausible structure. The central atom in most structures is usually less electronegative than the atoms that surround it.
3. Connect the atoms in the structure with single covalent bonds. Covalent bonds in Lewis dot structures are typically shown as a pair of dots.
4. Check whether each atom in the structure has a filled octet. Remember that hydrogen can only have two electrons, phosphorus can have eight or 10 electrons, and sulfur can have eight, 10, or 12 electrons. If all atoms have filled octets, skip to step (6). Otherwise, proceed to step (5).
5. If one or more atoms is left with an incomplete octet after step (4), share additional electrons between atoms to form more bonds. Do this to the extent necessary to give all atoms in period 2 complete octets.
6. Label any atoms that carry formal charges. When deciding between multiple valid Lewis dot structures, choose structures that minimize formal charges. Also, check to be sure that your structure contains the number of valence electrons that you calculated in step (1).

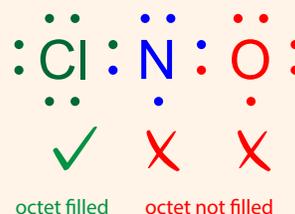
Example

Draw the Lewis dot structure of nitrosyl chloride (ClNO).

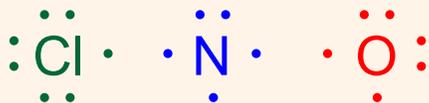
- ① Determine the number of valence electrons found in the structure:

$$\begin{array}{r}
 7 \text{ valence electrons from chlorine} \\
 5 \text{ valence electrons from nitrogen} \\
 + 6 \text{ valence electrons from oxygen} \\
 \hline
 \mathbf{18 \text{ total valence electrons}}
 \end{array}$$

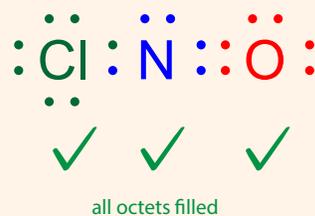
- ④ Check whether each atom has a filled octet.



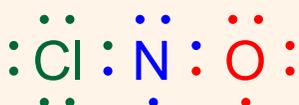
- ② Write the symbols for each atom and show their valence electrons. Let us pick nitrogen as the central atom, as nitrogen tends to form more bonds than oxygen or chlorine.



- ⑤ Form more bonds by sharing additional electrons until each atom has a filled octet.



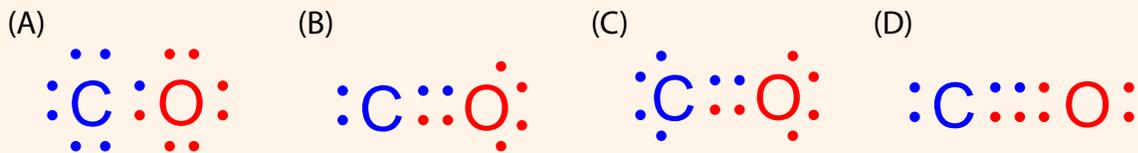
- ③ Share valence electrons to connect each atom with a single bond.



- ⑥ Check the answer by counting the number of valence electrons and ensure that formal charges are shown. Our structure is correct; it contains 18 valence electrons, and no atoms have formal charges.

Breakout

Which of the following Lewis dot structures for carbon monoxide (CO) contains the correct number of valence electrons and obeys the octet rule?



Complete the Lewis dot structure that you selected by labeling formal charges where appropriate.

Chemical bonds determine the geometry of atoms

The shape of a small molecule depends on the number of atoms in the molecule and the angles among those atoms. Generally speaking, the electrons in the bonds and lone pairs surrounding an atom repel one another and arrange so that they are kept as far apart as possible. Most of the elements that constitute the molecules of life assume one of three molecular geometries: tetrahedral, trigonal planar, or linear. A tetrahedron is a four-sided geometric solid in which each face is an equilateral triangle; when an atom adopts a **tetrahedral** geometry, the atom is positioned at the center of the tetrahedron and its four bonds and/or lone pairs point toward each of the four corners of the tetrahedron. Atoms with a total of four bonds and/or lone pairs adopt a tetrahedral geometry, as this geometry maximizes the distance among the electrons in each of its four substituents. If the tetrahedral geometry is perfectly symmetric, the angle between any two bonds made to the same central atom is about 109.5° (Figure 12A). Atoms with a total of three bonds and/or lone pairs adopt a **trigonal planar** geometry in which all three substituents and the central atom lie in the same plane, with the substituents at the maximum distance from each other. Trigonal planar geometry can be visualized as an equilateral triangle with the central atom at its center and the three substituents pointed towards the triangle's three corners. If the trigonal planar geometry is perfectly symmetric, the angle between any two bonds made to the same central atom is 120° (Figure 12B). Atoms with a total of two bonds and/or lone pairs adopt a **linear** geometry in which the two substituents are oriented on opposite sides of the central atom, such that the two substituents and

Figure 12 Tetrahedral and trigonal planar molecular geometry

(A) Atoms bound to four other atoms adopt a tetrahedral geometry. In this arrangement, the central atom lies at the center of a tetrahedron (*outlined in dashed lines*) whose corners are defined by the positions of the other four atoms. (B) Atoms bound to three other atoms adopt a trigonal planar geometry. In this arrangement, the central atom lies at the center of an equilateral triangle (*outlined in dashed lines*) whose corners are defined by the positions of the other three atoms.

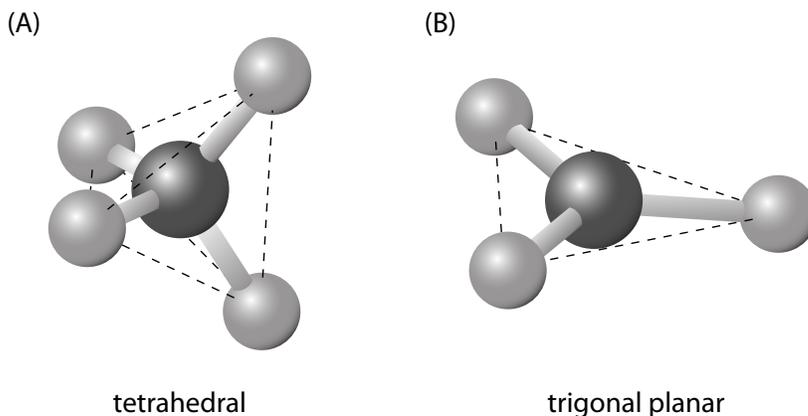
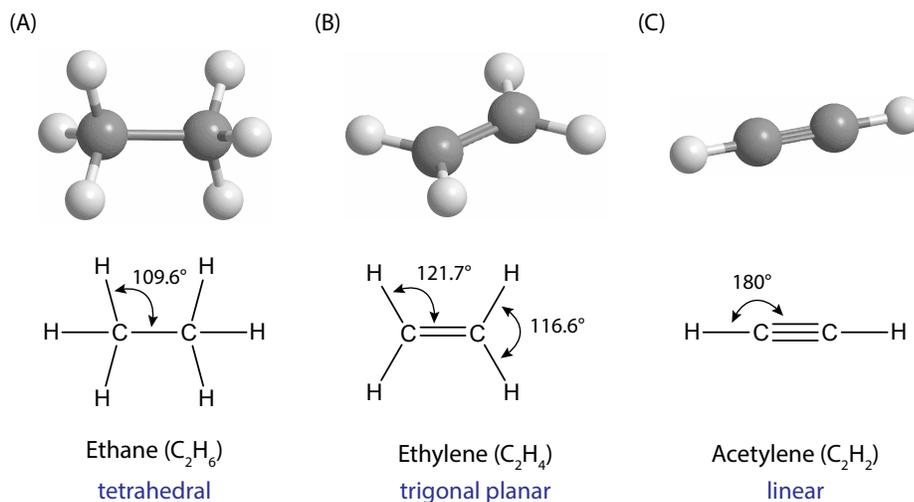


Figure 13 Double and triple bonds are treated as one bond in determining molecular geometry

Shown are three molecules all consisting of two carbon atoms and six (ethane in A), four (ethylene in B) or two (acetylene in C) hydrogen atoms. (A) When carbon forms bonds to four separate atoms (three hydrogens and the other carbon), it adopts a tetrahedral geometry. (B) When carbon forms two single bonds (to two hydrogens) and one double bond (to the other carbon), it adopts a trigonal geometry. (C) When carbon forms one single bond to a hydrogen and one triple bond to the other carbon, it adopts a linear geometry.



the central atom are collinear. The angle between the two bonds made to an atom with linear geometry is always 180° .

The bond angles found in real molecules can deviate from their ideal values when some bonds or lone pairs are more electron-rich, and therefore more repulsive, than others. For example, water has a tetrahedral geometry because of its two bonds and two lone pairs, but its hydrogen-oxygen-hydrogen bond angle is 104.45° instead of the ideal 109.5° . This difference exists because the electrons in the two lone pairs are closer to the oxygen atom than the electrons involved in the covalent bonds. As a result, the lone pairs repel one another more strongly than the covalent bonds do. Similar bond angle distortions are observed when atoms form both single and double bonds; since double bonds are shorter and more electron-rich, they repel other bonds and lone pairs more strongly than single bonds do (as seen in Figure 13).

Molecules can be represented with a variety of hand-drawn and computer-generated models

The widespread availability of computers makes accurate, three-dimensional models of organic molecules accessible to research scientists and students alike. Different styles of computer-generated models are used to represent organic molecules; these vary in complexity and are used to

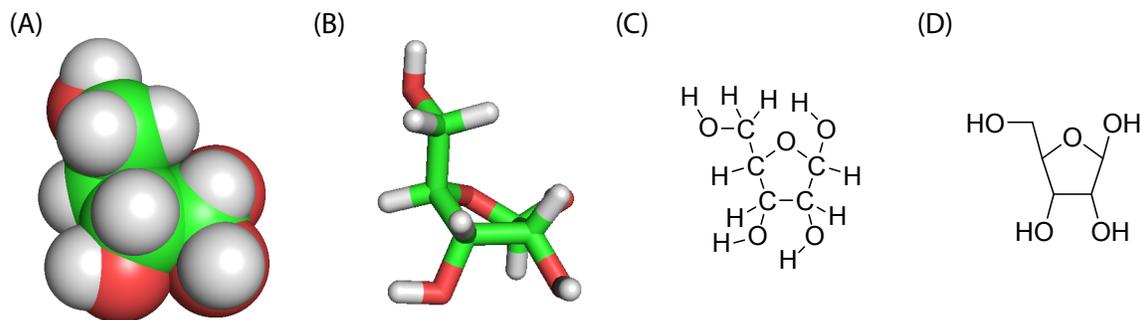


Figure 14 Different representations of ribose

This figure represents the molecule ribose in four ways. (A) Computer-generated space-filling model. (B) Computer-generated stick representation. (C) Extended line drawing showing all atoms and bonds. (D) Standard line drawing.

highlight specific molecular properties (Figure 14). **Stick representations** simply and clearly show the basic bonded structure of the molecule, but they provide little information about the physical space occupied by the molecule. In contrast, **space-filling models** are used to visualize the volume occupied by a molecule's electrons; however, this model's opacity often hides the molecule's important structural features. Space-filling models are often colored to show charges that are present on the surfaces of molecules, which can provide useful information about how that molecules interact and react with each other.

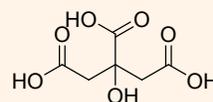
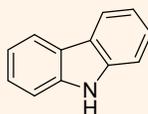
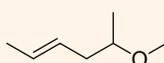
In many cases, computer-generated models are neither convenient nor necessary. Without the assistance of a computer, organic molecules can be drawn by hand in several different ways. Lewis structures are the most complete way to represent molecules, as they explicitly show the locations of each atom, bond, and electron pair, but chemists more often use the **standard line drawing** convention for depicting molecules (Box 3). Like Lewis structures, standard line drawings depict bonds as lines rather than as electron pairs; however, standard line drawings further simplify the

Box 3 Standard line drawings adhere to the following rules:

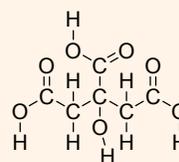
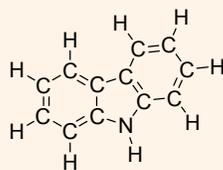
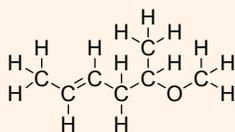
1. Lines are used to represent covalent bonds.
2. Intersections and termini of lines represent carbon atoms, but the symbol "C" for carbon is not explicitly shown.
3. Each carbon atom is bonded to enough hydrogen atoms to satisfy the octet rule (each neutral carbon atom must form four bonds in total). These hydrogen atoms are implied and are not explicitly shown.
4. All atoms other than carbon and hydrogen must be explicitly shown (e.g., P, O, N, Cl, etc.).
5. All hydrogen atoms that are bound to non-carbon atoms must be shown.
6. Lone pairs of electrons are not explicitly shown. It is implied that each atom has enough lone pair electrons to fill its octet.
7. Formal charges must be shown.

Shown below are several examples of standard line drawings (top row) and their corresponding extended molecular structures (bottom row).

Standard line drawings



Extended molecular structures
(all atoms and bonds shown)



representation by implying the presence of carbon and hydrogen atoms without explicitly showing them. While lone pairs are not required in standard line drawings, sometimes they are helpful to emphasize reactivity.

So far, we have introduced properties of atoms that derive from their electronic structures, and we have seen how covalent bonds between atoms give rise to the shapes of molecules. Covalent bonds (and any other kind of bond between atoms or interaction between molecules) do not just form and break randomly. Rather, the making and breaking of bonds within molecules is determined by the energetics of interactions between the constituent atoms. Likewise, interactions between molecules in the aqueous environment of the cell are governed by the same basic electrostatic forces that we have been considering. It is the energetics of these intermolecular interactions that we will consider next and that will begin to enable us to describe and understand the chemistry of a living cell, that is, its biology.

Summary

The electronic properties of atoms and molecules are the basis for life. Electrons in atoms are organized into shells and orbitals. Atoms are most stable when their outermost electron shell, or valence shell, is filled with electrons. To fill their valence shells, atoms can either gain or lose electrons or share electrons with other atoms. The effective nuclear charge experienced by an electron in an atom determines that atom's tendency to gain or lose electrons. Electronegativity, the tendency of an atom to attract electrons towards itself, is also determined by effective nuclear charge. Electronegativity can be quantified, and atoms near the top and right of the periodic table are most electronegative, whereas atoms towards the left and bottom are less electronegative. Highly electronegative atoms often fill their valence electron shells by gaining electrons to form negatively charged anions, whereas less-electronegative atoms often form positively charged cations by losing valence electrons. Ionic bonds form when two oppositely charged ions are attracted to one another and interact. Ionic bonds generally occur between atoms with large electronegativity differences.

Atoms can also fill their valence shells by forming covalent bonds, in which electrons are shared between two atoms. Covalent bonds always involve pairs of electrons; however, some covalent bonds involve the sharing of multiple pairs of electrons. Single, double, and triple bonds result from the sharing of one, two, and three pairs of electrons, respectively. The formation of bonds is favorable and releases energy. Conversely, breaking bonds requires energy, and the amount of energy required to break a bond is known as the bond dissociation energy.

Atoms most commonly found in living matter tend to form bonds until they have a total of eight valence electrons, a phenomenon known as the octet rule. Carbon, oxygen, and nitrogen always follow the octet rule. Hydrogen has fewer electron shells than those atoms, so it is most stable when it has a total of two valence electrons.

The shapes of molecules are determined by the number of bonds and lone electron pairs that each atom has. Atoms that have a total of four bonds and

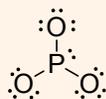
lone pairs adopt a tetrahedral geometry, atoms that have a total of three bonds and lone pairs adopt a trigonal geometry, and atoms that have a total of two bonds and lone pairs adopt a linear geometry.

Finally, the most exhaustive representation of a molecule is the Lewis dot structure, in which every atom, bond, and valence electron is explicitly shown. But scientists usually use the shortcut of standard line drawings. Standard line drawings do not explicitly show lone pairs of electrons, carbon atoms, or the hydrogen atoms that are bound to carbon atoms. Both Lewis dot structures and standard line drawings always show formal charges on charged atoms they may contain.

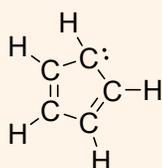
Practice problems

- Of the six elements commonly found in living things (S, P, O, N, C, and H), which is most electronegative? Which is least electronegative? How does electronegativity influence forces within and between molecules?
- Assign formal charges to the atoms in each of the following Lewis dot structures.

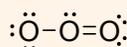
a.



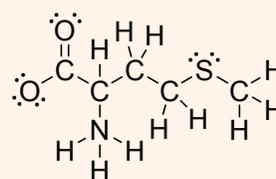
b.



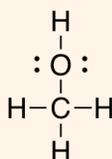
c.



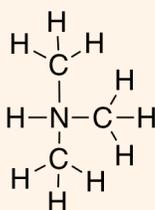
d.



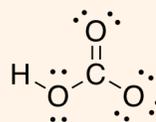
e.



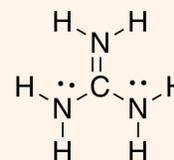
f.



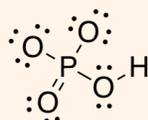
g.



h.



i.



- Draw Lewis dot structures for each of the following molecules.



(Solutions are located on the next page.)

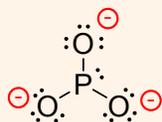
Solutions to practice problems

Question 1:

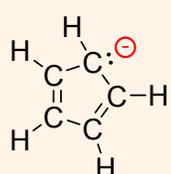
O is most electronegative; H is least electronegative. As we will see in the next chapter, electronegativity is important because it determines dipole interactions, which are important for intra- and intermolecular forces.

Question 2:

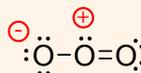
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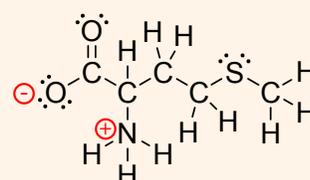
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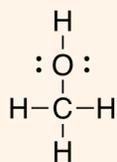
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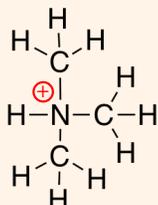
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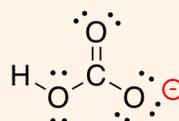
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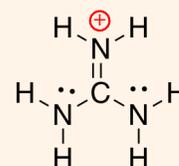
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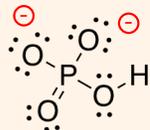
g.



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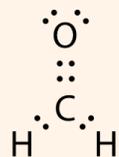


i.



Question 3:

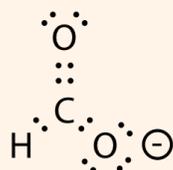
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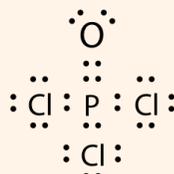
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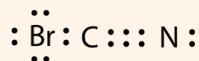
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