

More

Other Covalent Bonds

As noted earlier for H_2 , covalent bonds involving two $1s$ electrons are referred to as s bonds. Other atoms with single s electrons also form s -bonded molecules, e.g., K_2 and NaH . The dissociation energies and equilibrium separations for several s -bonded molecules are listed in Table 9-3. Notice that the strongest ones involve hydrogen and that two of these, NaH and LiH , also appear among the ionically bonded molecules in Table 9-2. They are examples of molecules that are mixtures of bonding types.

Atoms such as oxygen and nitrogen whose valence electrons occupy p states ($l = 1, m_l = +1, 0, -1$) can also form diatomic molecules via the covalent bond. Since there are six possible p states (i.e., three atomic orbitals) for each atom, there will be six molecular orbitals, each capable of being occupied by two electrons. (Closed shells do not participate significantly in molecular bonding and will be ignored in the following discussion.) In addition, there are a myriad of polyatomic molecules that are covalently bonded. Such molecules may be small or large, ranging from such relatively simple molecules as water, with molecular weight 18, through such giants as proteins, with molecular weights of up to 100,000 or perhaps even 1 million. As with diatomic molecules, the structure of such molecules can be understood by applying basic quantum mechanics to the bonding of the individual atoms. As you may imagine, characterization of the molecular orbitals can present a formidable problem, so

Table 9-3 Dissociation energies E_d and equilibrium separations r_0 for several covalent s -bonded molecules

Molecule	Dissociation energy (eV)	Equilibrium separation (nm)
H_2	4.52	0.074
Li_2	1.10	0.267
LiH	2.43	0.160
$LiNa$	0.91	0.281
Na_2	0.80	0.308
NaH	2.08	0.189
$NaRb$	0.61	0.359
K_2	0.59	0.392
KNa	0.66	0.347
Rb_2	0.47	0.422
Cs_2	0.43	0.450

Continued

we will direct our attention to a brief discussion of three applications of bonding involving p orbitals: pp homonuclear molecules such as O_2 ; sp directed bonds, of which H_2O is an example; and sp hybrid bonds, which occur in many molecules containing carbon.

By way of reminder, in Chapter 7 we solved the Schrödinger equation for the H atom and illustrated in Figure 7-11 the probability densities for the $l = 1$ electron states, these being a dumbbell-shaped distribution with maxima along the $+$ and $-$ z axis for the $l = 1, m_l = 0$ state and a toroidal-shaped distribution with its maximum in the xy plane for the $l = 1, m_l = \pm 1$ states. These wave functions have angular dependence proportional to $\cos \theta$ for $m_l = 0$ and $(\sin \theta)e^{\pm i\phi}$ for $m_l = \pm 1$. These results are, of course, not correct for other atoms, but the general features of the geometry are correct, so we will use them to help us understand the molecular p orbitals. It turns out to be more convenient for our purpose here to label the atomic p orbitals in terms of the spatial directions along which the probability densities have their maxima, rather than in terms of the value of the m_l quantum number. This is equivalent to picking particular linear combinations of solutions to the Schrödinger equation. These convenient combinations are called the p_x , p_y , and p_z atomic orbitals. The p_z orbital is just the atomic wave function with $m = 0$. The p_x and p_y orbitals are mixtures of the $m = \pm 1$ atomic wave functions. The angular dependence of these orbitals is

$$\begin{aligned}
 p_z &\propto \cos \theta \\
 p_x &\propto \sin \theta \left(\frac{e^{+i\phi} + e^{-i\phi}}{2} \right) = \sin \theta \cos \phi \\
 p_y &\propto \sin \theta \left(\frac{e^{+i\phi} - e^{-i\phi}}{2i} \right) = \sin \theta \sin \phi
 \end{aligned}
 \tag{9-4}$$

The electron charge distribution is maximum along the x , y , or z axes for these orbitals, as shown in Figure 9-9a. All three distributions are illustrated schematically in Figure 9-9b.

***pp* Bonds**

Let us first consider pp covalent bonding, which may occur when two atoms with electrons in the p shells approach one another. For simplicity we will consider atoms with $2p$ electrons. The explanation for $3p$, $4p$, etc., electrons is much the same, but involves keeping track of more molecular orbitals. While the two atoms may approach in any orientation and from any direction, let us assume arbitrarily that both are oriented as the one shown in Figure 9-9b and are approaching along their common z axis as sketched in Figure 9-10. As we described earlier for the case of H_2 , the possible superpositions of the $1s$ atomic wave functions lead to two $1s$ molecular orbitals, one bonding and the other antibonding as in Figure 9-8. Both $1s$ states are filled in each of our approaching atoms, so the two $1s$ molecular orbitals (see Figure 9-10), which can each hold two electrons, are both filled. The $2s$ atomic electron states also form bonding and antibonding molecular orbitals, and since the $2s$ states of both atoms were filled, so are the two molecular orbitals. Now look at the p atomic orbitals. These, too, form molecular p orbitals. As the atoms approach closely,

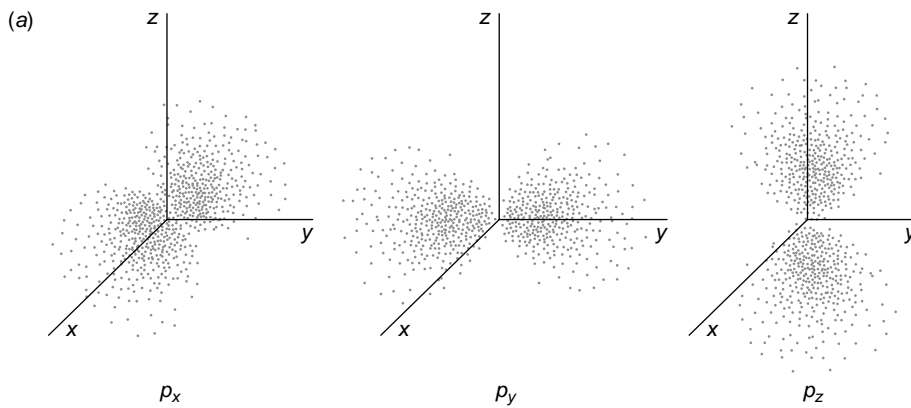


Fig. 9-9 (a) The p_x , p_y , and p_z atomic orbitals. [Computer-generated plots courtesy of Paul Doherty, *The Exploratorium*.] (b) Probability distribution of all three of the p atomic orbitals. The nucleus is at the origin.

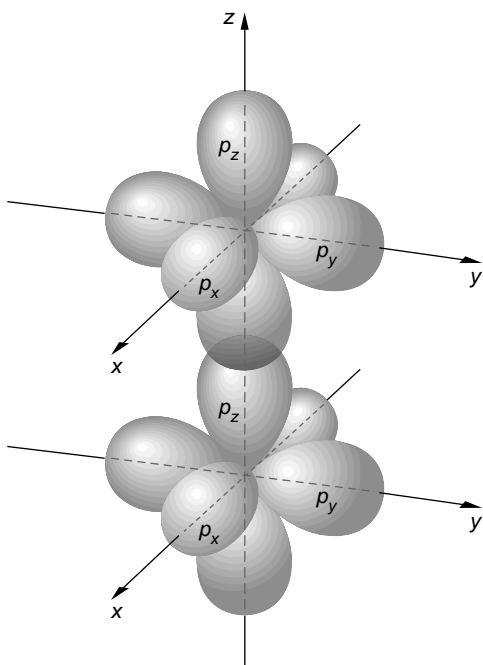
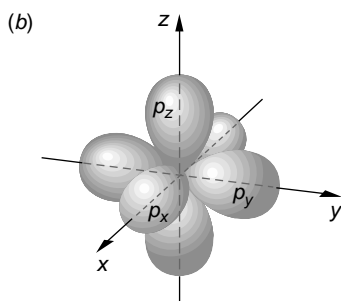


Fig. 9-10 Two atoms with $2p$ orbitals approach each other along their common z axis. Superposition of the symmetric wave functions leads to concentration of electron charge between the two nuclei and, thus, bonding molecular orbitals. Overlap of the antisymmetric atomic orbitals results in the antibonding molecular orbitals. The s orbitals are not shown.

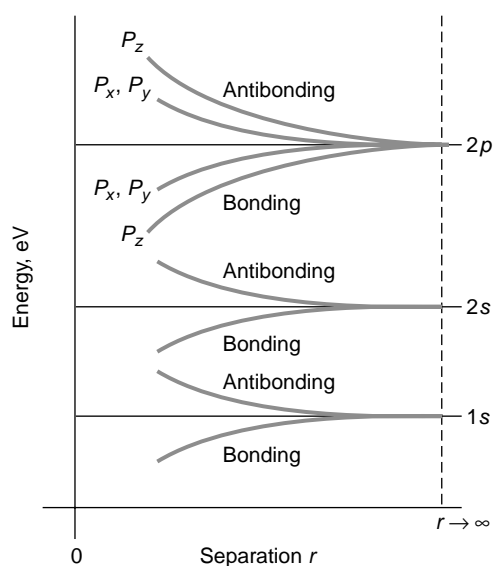


Fig. 9-II Energies of the bonding and antibonding molecular orbitals for atoms with $2p$ outer electrons. The diagram is not drawn to scale.

the p_z atomic orbitals begin to overlap significantly, much more so than the p_x and p_y orbitals, which are still rather far apart. Thus, the p_z orbitals will form bonding and antibonding molecular orbitals, much as the s states did. The p_x and p_y atomic orbitals also form molecular bonding and antibonding orbitals, but the p_z bonding orbital is lower in energy, and hence more stable, than the p_x and p_y bonding orbitals due to the former's larger overlap of the symmetric wave functions. Similarly, the p_z antibonding orbital, formed by overlapping antisymmetric wave functions, is of higher energy, and hence less stable, than the antibonding p_x and p_y orbitals, which have the same energy in our example. The several s and p molecular orbitals just described are illustrated in Figure 9-II.

Now we are able to understand the relative stabilities of diatomic molecules with pp covalent bonds. Nitrogen ($Z = 7$) has three $2p$ electrons; therefore, the N_2 molecule has six $2p$ electrons, enough to just fill the p_z , p_x and p_y molecular bonding orbitals. Thus, we expect the N_2 molecule to be very stable and chemically relatively unreactive, expectations which agree with observation (binding energy 9.8 eV and equilibrium separation 0.11 nm). Oxygen ($Z = 8$) has four $2p$ electrons; consequently, the O_2 molecule has eight electrons in p orbitals. The bonding p orbitals (see Figure 9-II) can hold only six of those, as was the case for the N_2 molecule, so two of the O_2 molecule's p electrons must occupy the next available state, the p_x or p_y antibonding orbital. We therefore expect O_2 to be less stable, i.e., more chemically reactive, than N_2 , an expectation which is again consistent with our experience. The binding energy of O_2 is substantially less than that of N_2 (see Table 9-4). The O_2

Table 9-4 Properties of pp -bonded molecules

	N_2	O_2	F_2
$2p$ electrons (total)	6	8	10
Binding energy (eV)	9.8	5.1	1.6
Equilibrium separation (nm)	0.11	0.12	0.14

Continued

molecular bonds can be broken by relatively low-energy chemical reactions. Fluorine ($Z = 9$), the next element after oxygen in the periodic table, has five $2p$ electrons. Thus, the F_2 molecule has 10 electrons in p orbitals, four of which must be in the antibonding p_x or p_y orbitals. Thus, we would expect F_2 to be less stable than O_2 , as indeed it is, undergoing violent reactions with many elements and compounds. In fact, its binding energy of 1.6 eV is at the lower end of the energy range of photons in the visible spectrum (about 1.6 eV to 3.3 eV); hence it is normally dissociated by exposure to light, a process called, not surprisingly, *photodissociation*.

We would expect behavior similar to that of the three molecules just discussed for their higher- Z counterparts with p -shell outer electrons. However, those corresponding to N_2 with np^3 structures (P, As, Sb, Bi) and those similar to O_2 with np^4 structures (S, Se, Te, Po) are all solids at room temperature. As we will see in Chapter 10, the interaction between atoms in solids tends to dominate and molecular bonding effects are not usually observed. The np^5 counterparts of F_2 (Cl, Br, I, At) are gases and all have properties similar to F_2 .

Finally, we do not expect neon (or the other noble gases Ar, Kr, Xe, Rn) to form covalently bonded molecules. The Ne_2 molecule would have 12 electrons in p orbitals, filling all of the antibonding orbitals. Perusal of the trend of binding energies in Table 9-4 leads us to expect a negative binding energy for Ne_2 , consistent with the experimental observation that neon does not form molecules.

sp Directed Bond

Many stable molecules are formed by *sp* covalent bonds, wherein one of the atoms has an s -state valence electron and the other has one or more p -state outer electrons. The mechanism is very similar to that discussed above and can be illustrated briefly with the HCl molecule. The $1s$ wave function for the H atom we have discussed previously. The Cl atom, like F, has five p electrons. This means that of the three $3p$ atomic orbitals, two are filled with pairs of electrons (with antiparallel spins) and the third contains a single unpaired electron. It is this unpaired electron that participates in the covalent bond. The four paired $3p$ electrons are not involved significantly, so we will ignore them. Schematically, the wave functions of the Cl unpaired $3p$ electron and the H $1s$ electron look as in Figure 9-12a as the two atoms approach one another, if it happens that the positive part of the $3p$ wave function is nearer the H atom. In that event the overlap of the wave functions results in an increased electron probability density between the two atoms, as Figure 9-12b illustrates, and an *sp* bonding orbital is formed. If, as the atoms approached each other, the negative part of the

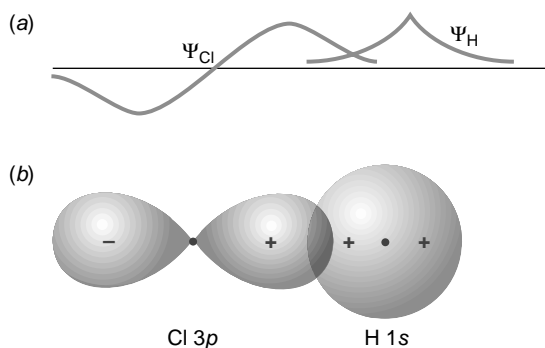


Fig. 9-12 (a) Schematic representation of the wave functions of the Cl $3p$ unpaired electron and the H $1s$ electron shown in the *sp* bonding orbital orientation. (b) The corresponding probability densities showing the overlap region where the higher probability of electron concentration (darkened region) leads to bonding.

$3p$ wave function had been closer to the H atom, an sp antibonding orbital would have been the result.

Now let us apply this result to the H_2O molecule. The maximum overlap of the electron wave functions occurs when two of the four oxygen $2p$ electrons are in one of the orbitals (e.g., p_z) with spins paired, one is in the p_x orbital, and the other is in the p_y orbital. Each of the unpaired electrons in the p_x and p_y orbitals forms an sp bond with a hydrogen atom electron. If it were not for the Coulomb repulsion of the two H nuclei, we would therefore expect the O—H bonds to be at right angles to one another, i.e., one along the x axis and the other along the y axis. The effect of this repulsion can be calculated, and the result is in agreement with the measured angle of 104.5° (see Figure 9-13).

As we have previously mentioned, the electrons that participate in the bonding are not confined to their original atoms, but instead are shared by both atoms. A complete description of the molecular charge distribution would therefore require the use of molecular orbitals rather than the atomic orbitals given in Equation 9-4. However, the resultant molecular orbitals have much the same character as the atomic orbitals.

Similar reasoning leads to an understanding of the bonding in the ammonia molecule, NH_3 . The ground-state configuration of nitrogen is $1s^2 2s^2 2p^3$. Maximum overlap of bonding-electron wave functions is achieved when the three electrons in the p state of nitrogen are unpaired in the p_x , p_y , and p_z orbitals. Each of the $3p$ electrons participates in a directed sp bond with a hydrogen atom electron to form the three-dimensional structure shown in Figure 9-14. Again, because of the repulsion of the hydrogen atoms, the angles between the bonds are somewhat larger than 90° : in this case the angle is 107.3° . The structure is a pyramid, with the nitrogen atom at the vertex and the three hydrogen atoms at the base. The bond angle should decrease for larger Z , np^3 atoms replacing nitrogen, since the H atoms will be relatively farther apart, reducing their mutual repulsion.

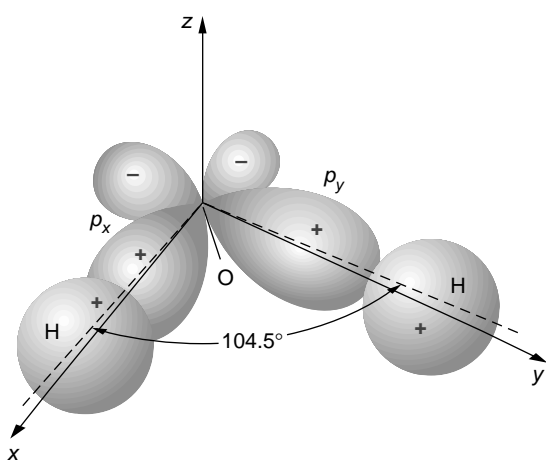


Fig. 9-13 Electron charge distribution of the sp bonding orbitals in the H_2O molecule.

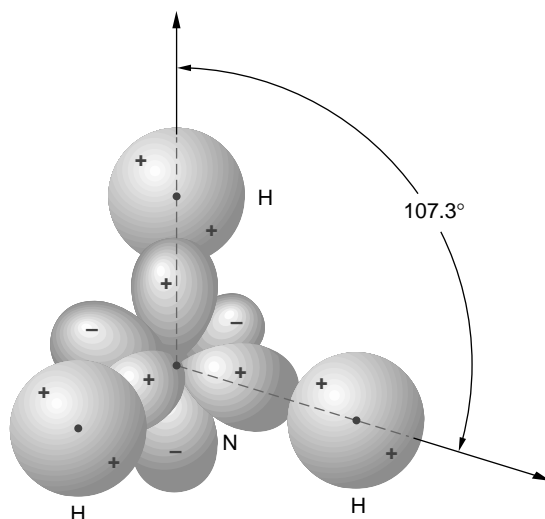


Fig. 9-14 Schematic diagram of the wave functions showing overlap for the $2p$ electrons of N and the $1s$ electron of H that participate in the directed sp bonding of the NH_3 molecule. The + and - signs refer to the relative signs of the wave functions.

Table 9-5 Dissociation energy and equilibrium separation of *sp*-bonded molecules

Molecule	Dissociation energy (eV)	Equilibrium separation (nm)
HF	5.90	0.092
HCl	4.48	0.128
HBr	3.79	0.141
HI	3.10	0.160
LiF	5.98	0.156
LiCl	4.86	0.202
LiI	3.67	0.238
NaF	4.99	0.193
NaCl	4.26	0.236
NaBr	3.76	0.253
KF	5.15	0.217
KCl	4.43	0.267

In Table 9-5 are listed the properties of several diatomic *sp*-bonded molecules. Notice that once again several of these also appear among the ionically bonded molecules listed in Table 9-2. The bond angles of several polyatomic directed *sp*-bonded molecules are listed in Table 9-6. These are arranged in two groups: one with two H atoms per molecule and the other with three H atoms per molecule. Within each group the molecules are arranged in order of increasing atomic number *Z* of the atom providing the *p* electrons to the bond. As you would expect from the discussion above, within each group the bond angle approaches 90° as *Z* becomes large.

Table 9-6 Bond angles of directed *sp*-bonded polyatomic molecules

Molecule	Bond angle (°)	Molecule	Bond angle (°)
H ₂ O	104.5	NH ₃	107.3
H ₂ S	93.3	PH ₃	93.3
H ₂ Se	91.0	AsH ₃	91.8
H ₂ Te	89.5	SbH ₃	91.3

sp Hybrid Bonds

As our final example, we consider the more complicated but very important case of the bonding of carbon atoms to hydrogen and other atoms. Although carbon is a *2p* atom, we did not include it in our earlier discussion for a special reason, as we will explain. The ground-state configuration of carbon is $1s^2 2s^2 2p^2$. From our previous discussion we might expect carbon to be divalent, with the two *2p* electrons forming bonds at approximately 90° like the oxygen atom to form molecules like CH₂ with directed *sp* bonds like H₂O. The most important experimental feature of carbon

chemistry, however, is that tetravalent carbon compounds such as CH_4 in which the four bonds are equivalent are overwhelmingly favored. Similarly, we expect elements such as B, Al, and Ga, all with a single p electron, to form molecules like BCl , B_2O , Al_2O , and GaF . Instead, they behave as if they have three valence electrons, forming molecules such as BCl_3 and Al_2O_3 .

The observed valence of 4 for carbon comes about in an interesting way. One of the first excited states of carbon occurs when a $2s$ electron is excited to a $2p$ state, giving a configuration of $1s^2 2s^1 2p^3$ for this state. In this excited state we can have four unpaired electrons, one each in the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. If the four bonding electrons were described by these atomic orbitals, we would expect there to be three similar bonds at angles of about 90° and one somewhat different bond corresponding to the $2s$ orbital, which has no directional character. The four wave functions corresponding to these four atomic orbitals have approximately but not exactly the same energy. Again, this is not what is observed. However, it is possible to find four linear combinations of these orbitals that do have the same energy and that have the necessary directional characteristics to describe the observed bonding of carbon. These *hybrid* wave functions are of the form

$$\begin{aligned}\psi_1 &= \frac{1}{2}(s + p_x + p_y + p_z) \\ \psi_2 &= \frac{1}{2}(s + p_x - p_y - p_z) \\ \psi_3 &= \frac{1}{2}(s - p_x - p_y + p_z) \\ \psi_4 &= \frac{1}{2}(s - p_x + p_y - p_z)\end{aligned}\quad \mathbf{9-5}$$

These are called the sp^3 hybrid orbitals.

This mixing of atomic orbitals, called *hybridization*, is probably the single most important new feature involved in the physics of complex molecular bonds. Figure 9-15 shows the tetrahedral structure of the methane (CH_4) molecule, and Figure 9-16 shows the ethane molecule ($\text{CH}_3\text{—CH}_3$), which is similar to CH_4 except that one of the C—H bonds is replaced by a C—C bond.

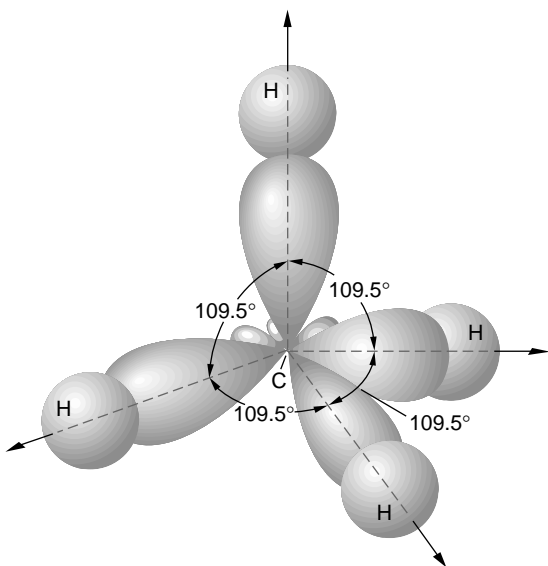


Fig. 9-15 Electron charge distribution in the CH_4 molecule (methane).

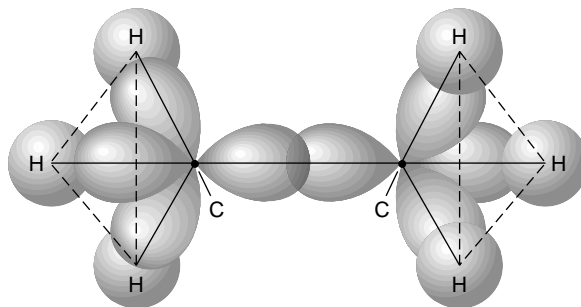


Fig. 9-16 Electron charge distribution in the C_2H_6 molecule (ethane).

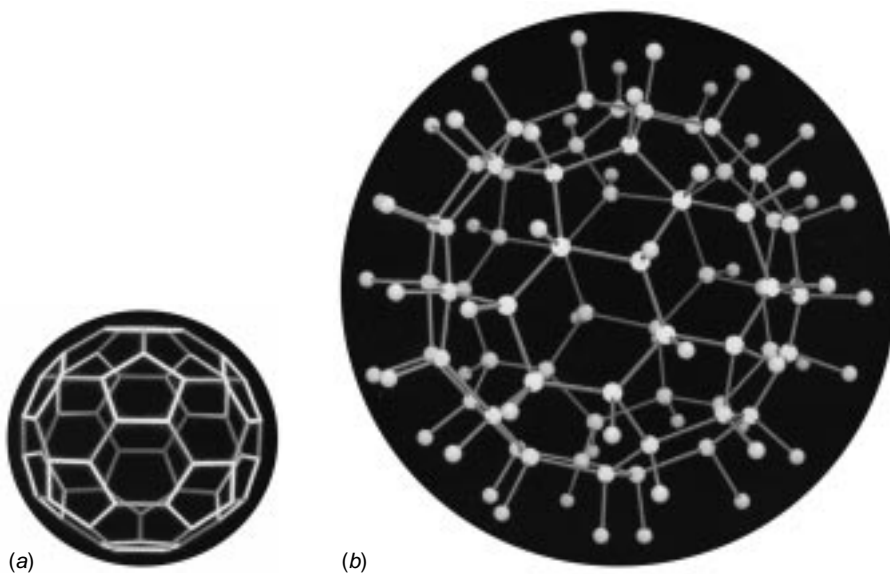


Fig. 9-17 (a) Schematic representation of buckminsterfullerene, the C_{60} molecule. (b) The bonding of an H atom to each of the sixty C atoms of the buckyball, predicted but not yet seen, will produce the "fuzzyball." [Parts (a) and (b) from Ian Worpole, *Scientific American* 265 (4), October 1991, p. 56.]

Carbon orbitals can also hybridize in the sp^2 configuration, in which the s , p_x , and p_y orbitals combine to form three hybrid orbitals in the xy plane with 120° bonds and the p_z orbital remains unmixed. Examples of this configuration include graphite, where the xy plane bonds provide the strongly layered structure characteristic of the material, and organic molecules such as ethylene ($H_2C=CH_2$) and benzene (C_6H_6).

The hybrid sp^2 covalent bond in carbon is also the mechanism by which the group of carbon molecules called *fullerenes* are formed. The first fullerene was identified in 1985 when the C_{60} molecule was discovered. Called buckminsterfullerene,³ this remarkable molecule is a spheroid with a structure having the perfect symmetry of a soccer ball, i.e., a closed network of pentagons and hexagons. A carbon atom is located at each corner of the hexagons. Because of this similarity in structure, C_{60} is often referred to as "buckyball." (See Figure 9-17a.) The eighteenth-century mathematician Leonhard Euler⁴ had calculated that any such object, in order to close into a spheroid, must have exactly 12 pentagons, although the number of hexagons can vary widely. C_{60} has 20 hexagons of carbon atoms. The diameter of a buckyball is 0.71 nm. Shortly after the discovery of C_{60} , another fullerene of nearly equal stability, C_{70} , was discovered. Since then, fullerenes from C_{32} up to C_{960} have been found, the former whimsically called "buckybabies" and the latter among the giant fullerenes. The double bonds ($C=C$) available in the hybrid sp^2 structure enable numerous molecules to be formed with other atoms (see Figure 9-17b), the extent of which has only begun to be explored. The properties of solid fullerenes, which are equally remarkable, will be discussed in Chapter 10.

We do not have the space to discuss further the many interesting features of the molecular bonding in carbon compounds. The great family of carbon compounds, known as *organic* compounds because of their close connection with the chemistry of living things, arises not from different underlying principles but rather from carbon's ready hybridization to give bonds that may be incorporated into molecules of great diversity. Despite the complexity of polyatomic molecules, their features can be understood in the framework of the principles of quantum mechanics discussed in the previous chapters.