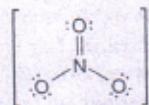


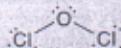
Solution

The following Lewis structure shows one of the three resonance structures of the nitrate ion:



Because the central nitrogen atom has no lone pairs and the three oxygens are equivalent, the nitrate ion should be planar with a 120° bond angle. This is the observed structure.

The Lewis structure for OCl_2 is



The central oxygen atom is surrounded by two ligands and two lone pairs. The ligands and lone pairs are described by a distorted tetrahedral arrangement, leading to a bent molecule. The bond angle should be near the tetrahedral angle of 109.5° . The observed bond angle is 111° .

25.2 Describing Localized Bonds Using Hybridization for Methane, Ethene, and Ethyne

As discussed earlier, the VSEPR model is useful in predicting the shape of a wide variety of molecules. Although the model is based on quantum mechanical results, the rules used in its application do not specifically use the vocabulary of quantum mechanics. However, VB theory, which was discussed in Chapter 23, does use the concept of localized orbitals to explain molecular structure. In the VB model, AOs on the same atom are combined to generate a set of directed orbitals in a process called **hybridization**. The combined orbitals are referred to as **hybrid orbitals**. In keeping with a local picture of bonding, the hybrid orbitals need to contribute independently to the electron density and to the energy of the molecule to the maximum extent possible, because this allows the assembly of the molecule out of separate and largely independent parts. This requires the set of hybrid orbitals to be orthogonal.

How is hybridization used to describe molecular structure? Consider the sequence of molecules methane, ethene, and ethyne. From previous chemistry courses, you know that carbon in these molecules is characterized by the sp^3 , sp^2 , and sp hybridizations, respectively. What is the functional form associated with these different hybridizations? We construct the hybrid orbitals for ethene to illustrate the procedure.

To model the three σ bonds in ethene, the carbon AOs are hybridized to the configuration $1s^2 2p_z^1 (\psi_a)^1 (\psi_b)^1 (\psi_c)^1$ rather than to the configuration $1s^2 2s^2 2p^2$, which is appropriate for an isolated carbon atom. The orbitals ψ_a , ψ_b , and ψ_c are the wave functions that are used in a valence bond model for the three σ bonds in ethene. We next formulate ψ_a , ψ_b , and ψ_c in terms of the $2s$, $2p_x$, and $2p_z$ AOs on carbon.

The three sp^2 -hybrid orbitals ψ_a , ψ_b , and ψ_c must satisfy the geometry shown schematically in Figure 25.3. They lie in the x - z plane and are oriented at 120° to one another. The appropriate linear combination of carbon AOs is

$$\begin{aligned}\psi_a &= c_1 \phi_{2p_z} + c_2 \phi_{2s} + c_3 \phi_{2p_x} \\ \psi_b &= c_4 \phi_{2p_z} + c_5 \phi_{2s} + c_6 \phi_{2p_y} \\ \psi_c &= c_7 \phi_{2p_z} + c_8 \phi_{2s} + c_9 \phi_{2p_x}\end{aligned}\quad (25.1)$$

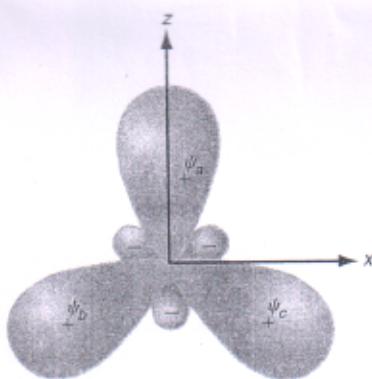


FIGURE 25.3

Geometry of the sp^2 -hybrid orbitals used in Equation (25.1). In this and in most of the figures in this chapter, we use a “slimmed down” picture of hybrid orbitals to separate individual orbitals. A more correct form for $s-p$ hybrid orbitals is shown in Figure 25.5.

How can c_1 through c_9 be determined? A few aspects of the chosen geometry simplify the task of determining the coefficients. Because the $2s$ orbital is spherically symmetrical, it will contribute equally to each of the hybrid orbitals. Therefore, $c_2 = c_5 = c_8$. These three coefficients must satisfy the equation $\sum_i (c_{2s})^2 = 1$, where the subscript $2s$ refers to the $2s$ AO. This equation states that all of the $2s$ contributions to the hybrid orbitals must be accounted for. We choose $c_2 < 0$ in the preceding equations to make the $2s$ orbital,

$$\psi_{200}(r) = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_0} \right)^{3/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

have a positive amplitude in the bonding region. (For graphs of the $2s$ AO amplitude versus r , see Figures 20.5 and 20.6.) Therefore, we conclude that

$$c_2 = c_5 = c_8 = -\frac{1}{\sqrt{3}}$$

From the orientation of the orbitals seen in Figure 25.3, $c_3 = 0$ because ψ_a is oriented on the z axis. Because the hybrid orbital points along the positive z axis, $c_1 > 0$. We can also conclude that $c_4 = c_7$, that both are negative, and that $-c_6 = c_9$ with $c_9 > 0$. Based on these considerations, Equation (25.1) simplifies to

$$\psi_a = c_1 \phi_{2p_z} - \frac{1}{\sqrt{3}} \phi_{2s} \quad (25.2)$$

$$\psi_b = c_4 \phi_{2p_z} - \frac{1}{\sqrt{3}} \phi_{2s} - c_6 \phi_{2p_x}$$

$$\psi_c = c_4 \phi_{2p_z} - \frac{1}{\sqrt{3}} \phi_{2s} + c_6 \phi_{2p_y}$$

As shown in Example Problem 25.2, the remaining unknown coefficients can be determined by normalizing and orthogonalizing ψ_a , ψ_b , and ψ_c .

EXAMPLE PROBLEM 25.2

Determine the three unknown coefficients in Equation (25.2) by normalizing and orthogonalizing the hybrid orbitals.

Solution

We first normalize ψ_a . Terms such as $\int \phi_{2p_z}^* \phi_{2p_z} d\tau$ and $\int \phi_{2s}^* \phi_{2p_z} d\tau$ do not appear in the following equations because all of the AOs are orthogonal to one another. Evaluation of the integrals is simplified because the individual AOs are normalized.

$$\begin{aligned} \int \psi_a^* \psi_a d\tau &= (c_1)^2 \int \phi_{2p_z}^* \phi_{2p_z} d\tau + \left(-\frac{1}{\sqrt{3}} \right)^2 \int \phi_{2s}^* \phi_{2s} d\tau = 1 \\ &= (c_1)^2 + \frac{1}{3} = 1 \end{aligned}$$

which tells us that $c_1 = \sqrt{2/3}$. Orthogonalizing ψ_a and ψ_b we obtain

$$\int \psi_a^* \psi_b d\tau = c_4 \sqrt{\frac{2}{3}} \int \phi_{2p_z}^* \phi_{2p_z} d\tau + \left(-\frac{1}{\sqrt{3}} \right)^2 \int \phi_{2s}^* \phi_{2s} d\tau = 0$$

$$= c_4 \sqrt{\frac{2}{3}} + \frac{1}{3} = 0 \quad \text{and}$$

$$c_4 = -\sqrt{\frac{1}{6}}$$

Normalizing ψ_b , we obtain

$$\begin{aligned}\int \psi_b^* \psi_b d\tau &= \left(-\sqrt{\frac{1}{6}}\right)^2 \int \phi_{2p_z}^* \phi_{2p_z} d\tau + \left(-\frac{1}{\sqrt{3}}\right)^2 \int \phi_{2s}^* \phi_{2s} d\tau + (-c_6)^2 \int \phi_{2p_x}^* \phi_{2p_x} d\tau \\ &= (c_6)^2 + \frac{1}{3} + \frac{1}{6} = 1 \quad \text{and} \\ c_6 &= +\sqrt{\frac{1}{2}}\end{aligned}$$

We have chosen the positive root so that the coefficient of ϕ_{2p_x} in ψ_b is negative. Using these results, the normalized and orthogonal set of hybrid orbitals is

$$\begin{aligned}\psi_a &= \sqrt{\frac{2}{3}} \phi_{2p_z} - \frac{1}{\sqrt{3}} \phi_{2s} \\ \psi_b &= -\sqrt{\frac{1}{6}} \phi_{2p_z} - \frac{1}{\sqrt{3}} \phi_{2s} - \sqrt{\frac{1}{2}} \phi_{2p_x} \\ \psi_c &= -\sqrt{\frac{1}{6}} \phi_{2p_z} - \frac{1}{\sqrt{3}} \phi_{2s} + \sqrt{\frac{1}{2}} \phi_{2p_x}\end{aligned}$$

Convince yourself that ψ_c is normalized and orthogonal to ψ_a and ψ_b .

How can the 2s and 2p character of the hybrids be quantified? Because the sum of the squares of the coefficients for each hybrid orbital equals one, the p and s character of the hybrid orbital can be calculated. The fraction of 2p character in ψ_b is $\frac{1}{6} + \frac{1}{2} = \frac{2}{3}$. The fraction of 2s character is 1/3. Because the ratio of the 2p to 2s character is 2:1, one refers to sp^2 hybridization.

How do we know that these hybrid orbitals are oriented with one another as shown in Figure 25.3? Because ψ_a has no component of the $2p_x$ orbital, it must lie on the z axis, corresponding to a value of zero for the polar angle θ . To demonstrate that the ψ_b orbital is oriented as shown, we find its maximum value with respect to the variable θ , which is measured from the z axis (see Figure 13.4).

EXAMPLE PROBLEM 25.3

Demonstrate that the hybrid orbital ψ_b has the orientation shown in Figure 25.3.

Solution

To carry out this calculation, we have to explicitly include the θ dependence of the $2p_x$ and $2p_z$ orbitals from Chapter 20. In doing so, we set the azimuthal angle ϕ , discussed in Section 20.3, equal to zero:

$$\frac{d\psi_b}{d\theta} = \left[\frac{1}{\sqrt{32\pi}} \left(\frac{\zeta}{a_0} \right)^{3/2} e^{-\zeta r/2a_0} \right] \frac{d}{d\theta} \left(-\sqrt{\frac{1}{6}} \frac{\zeta r}{a_0} \cos \theta - \sqrt{\frac{1}{3}} \left[2 - \frac{\zeta r}{a_0} \right] - \sqrt{\frac{1}{2}} \frac{\zeta r}{a_0} \sin \theta \right) = 0$$

which simplifies to

$$\sqrt{\frac{1}{6}} \sin \theta - \sqrt{\frac{1}{2}} \cos \theta = 0 \quad \text{or} \quad \tan \theta = \sqrt{3}$$

This value for $\tan \theta$ is satisfied by $\theta = 60^\circ$ and 240° . Applying the condition that $d^2\psi_b/d\theta^2 < 0$ for the maximum, we conclude that $\theta = 240^\circ$ corresponds to the maximum and $\theta = 60^\circ$ corresponds to the minimum. Similarly, it can be shown that ψ_c has its maximum value at 120° and a minimum at 300° .

TABLE 25.1

C—C Bond Types

| Carbon—Carbon Bond Types | σ Bond Hybridization | s-to-p Ratio | Angle between Equivalent σ Bonds ($^\circ$) | Carbon—Carbon Single Bond Length (pm) |
|--------------------------|-----------------------------|--------------|--|---------------------------------------|
| | sp^3 | 1:3 | 109.4 | 154 |
| | sp^2 | 1:2 | 120 | 146 |
| | sp | 1:1 | 180 | 138 |

Example Problem 25.3 shows that sp^2 hybridization generates three equivalent hybrid orbitals that are separated by an angle of 120° . By following the procedure outlined earlier, it can be shown that the set of orthonormal sp -hybrid orbitals that are oriented 180° apart is

$$\psi_a = \frac{1}{\sqrt{2}}(-\phi_{2s} + \phi_{2p_z}) \quad (25.3)$$

$$\psi_b = \frac{1}{\sqrt{2}}(-\phi_{2s} - \phi_{2p_z})$$

and that the set of tetrahedrally oriented orthonormal hybrid orbitals for sp^3 hybridization that are oriented 109.4° apart is

$$\psi_a = \frac{1}{2}(-\phi_{2s} + \phi_{2p_x} + \phi_{2p_y} + \phi_{2p_z}) \quad (25.4)$$

$$\psi_b = \frac{1}{2}(-\phi_{2s} - \phi_{2p_x} - \phi_{2p_y} + \phi_{2p_z})$$

$$\psi_c = \frac{1}{2}(-\phi_{2s} + \phi_{2p_x} - \phi_{2p_y} - \phi_{2p_z})$$

$$\psi_d = \frac{1}{2}(-\phi_{2s} - \phi_{2p_x} + \phi_{2p_y} - \phi_{2p_z})$$

By combining s and p orbitals, at most four hybrid orbitals can be generated. To describe bonding around a central atom with coordination numbers greater than four, d orbitals need to be included in forming the hybrids. Although hybrid orbitals with d character are not discussed here, the principles used in constructing them are the same as those outlined earlier.

The properties of C—C single bonds depend on the hybridization of the carbon atoms, as shown in Table 25.1. The most important conclusion that can be drawn from this table for the discussion in the next section is that increasing the s character in $s-p$ hybrids increases the bond angle. Note also that the C—C single bond length becomes shorter as the s character of the hybridization increases, and that the C—C single bond energy increases as the s character of the hybridization increases.

25.3 Constructing Hybrid Orbitals for Nonequivalent Ligands

In the preceding section, the construction of hybrid orbitals for equivalent ligands was considered. However, in general, molecules contain nonequivalent ligands as well as nonbonding electron lone pairs. How can hybrid orbitals be constructed for such molecules if

the bond angles are not known? By considering the experimentally determined structures of a wide variety of molecules, Henry Bent formulated the following guidelines:

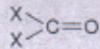
- Central atoms that obey the octet rule can be classified into three structural types. Central atoms that are surrounded by a combination of four single bonds or electron pairs are to a first approximation described by a tetrahedral geometry and sp^3 hybridization. Central atoms that form one double bond and a combination of two single bonds or electron pairs are to a first approximation described by a trigonal geometry and sp^2 hybridization. Central atoms that form two double bonds or one triple bond and either a single bond or an electron pair are to a first approximation described by a linear geometry and sp hybridization.
- The presence of different ligands is taken into account by assigning a different hybridization to all nonequivalent ligands and lone pairs. The individual hybridization is determined by the electronegativity of each ligand. A nonbonding electron pair can be considered to be electropositive or, equivalently, to have a small electronegativity. Bent's rule states that atomic s character concentrates in hybrid orbitals directed toward electropositive ligands and that p character concentrates in hybrid orbitals directed toward electronegative ligands.

We now apply these guidelines to H_2O . The oxygen atom in H_2O is to a first approximation described by a tetrahedral geometry and sp^3 hybridization. However, because the H atoms are more electronegative than the electron pairs, the p character of the hybrid orbitals directed toward the hydrogen atoms will be greater than that of sp^3 hybridization. Because Table 25.1 shows that increasing the p character decreases the bond angle, Bent's rule says that the H—O—H bond angle will be less than 109.4° . Note that the effect of Bent's rule is the same as the effect of the VSEPR rules listed in Section 25.1. However, the hybridization model provides a basis for the rules.

Although useful in predicting bond angles, Bent's rule is not quantitative. To make it predictive, a method is needed to assign a hybridization to a specific combination of two atoms that is independent of the other atoms in the molecule. Several authors have developed methods that meet this need, for example, D. M. Root *et al.* in *J. American Chemical Society* 115 (1993), 4201–4209.

EXAMPLE PROBLEM 25.4

- a. Use Bent's rule to estimate the change in the X—C—X bond angle in

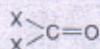


when going from H_2CO to F_2CO .

- b. Use Bent's rule to estimate the deviation of the H—C—H bond angle in FCH_3 and ClCH_3 from 109.4° .

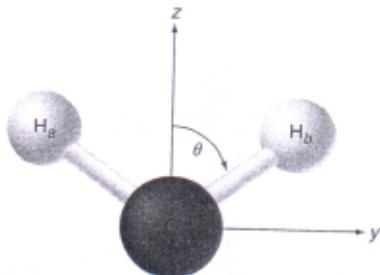
Solution

- a. To first order, the carbon atom in



should exhibit sp^2 hybridization. Because F is more electronegative than H, the hybridization of the C—F ligand contains more p character than does the C—H ligand. Therefore, the F—C—F bond angle will be smaller than the H—C—H bond angle.

- b. Using the same argument as in part (a), the H—C—H bond angles in both compounds will be smaller than 109.4° . The angle will be larger in FCH_3 than in ClCH_3 .

**FIGURE 25.4**

Coordinate system used to generate the hybrid orbitals on the oxygen atom that are suitable for describing the structure of H_2O .

To test the predictions of Bent's rule, the hybrid bonding and lone pair orbitals for water are constructed, using the known bond angle, and their individual hybridizations are determined. The configuration of the water molecule can be written in the form $1s_{\text{oxygen}}^2 (\psi_{OH})^2 (\psi_{OH})^2 (\psi_{\text{lone pair}})^2 (\psi_{\text{lone pair}})^2$. Each ψ_{OH} and $\psi_{\text{lone pair}}$ describes localized hybrid orbitals. From the known geometry, the two bonding orbitals are oriented at 104.5° with respect to one another, as shown in Figure 25.4. In constructing the hybrids, the lone pair and bond orbitals are required to maximize their angular separation. Starting with this input, how do we construct ψ_{OH} and $\psi_{\text{lone pair}}$ starting with the atomic orbitals on hydrogen and oxygen? To describe the H_2O molecule, a pair of orthogonal equivalent $s-p$ hybrids, called ψ_a and ψ_b , is constructed on the oxygen atom. The calculation is initially carried out for an arbitrary angle.

The hybrid orbitals are described by

$$\psi_a = N \left[\cos \theta \phi_{2p_z} + \sin \theta \phi_{2p_y} - \alpha \phi_{2s} \right] \quad (25.5)$$

$$\psi_b = N \left[\cos \theta \phi_{2p_z} - \sin \theta \phi_{2p_y} - \alpha \phi_{2s} \right]$$

where N is a normalization constant and α is the relative amplitude of the $2s$ and $2p$ orbitals.

To derive this equation, visualize ϕ_{2p_z} and ϕ_{2p_y} as vectors along the y and z directions. Because the $2s$ orbital has one radial node, the $2s$ orbital coefficient in Equation (25.5) is negative, which generates a positive amplitude at the position of the H atom. The two hybrid orbitals are orthogonal only if

$$\begin{aligned} \int \psi_a^* \psi_b d\tau &= N^2 \int \left[\cos \theta \phi_{2p_z} + \sin \theta \phi_{2p_y} - \alpha \phi_{2s} \right] \left[\cos \theta \phi_{2p_z} - \sin \theta \phi_{2p_y} - \alpha \phi_{2s} \right] d\tau \quad (25.6) \\ &= N^2 \left[\cos^2 \theta \int \phi_{2p_z}^* \phi_{2p_z} d\tau - \sin^2 \theta \int \phi_{2p_y}^* \phi_{2p_y} d\tau + \alpha^2 \int \phi_{2s}^* \phi_{2s} d\tau \right] = 0 \end{aligned}$$

Terms such as $\int \phi_{2p_y}^* \phi_{2p_z} d\tau$ and $\int \phi_{2s}^* \phi_{2p_y} d\tau$ do not appear in this equation because all of the atomic orbitals are orthogonal to one another. Because each of the AOs is normalized, Equation (25.6) reduces to

$$\begin{aligned} N^2 [\cos^2 \theta - \sin^2 \theta + \alpha^2] &= N^2 [\cos 2\theta + \alpha^2] = 0 \quad \text{or} \quad (25.7) \\ \cos 2\theta &= -\alpha^2 \end{aligned}$$

In simplifying this equation, we have used the identity $\cos^2 x - \sin^2 y = \cos(x+y)\cos(x-y)$. Because $\alpha^2 > 0$, $\cos 2\theta < 0$ and the bond angle $180^\circ \geq 2\theta \geq 90^\circ$. What has this calculation shown? We have demonstrated that it is possible to create two hybrid orbitals separated by a bonding angle in this angular range simply by varying the relative contributions of the $2s$ and $2p$ orbitals to the hybrid. Discussion of the energy cost of hybridization is deferred until later in this section.

The hybrid orbitals in Equation (25.5) are not specific to a particular molecule other than that the two atoms that bond to the central oxygen atom are identical. We now calculate the value of α that generates the correct bond angle in H_2O and also describe the lone pairs around the oxygen atom. Calculating α by substituting the known value $\theta = 52.25^\circ$ in Equation (25.7), we find that the unnormalized hybrid orbitals that describe bonding in water are

$$\psi_a = N[0.61\phi_{2p_z} + 0.79\phi_{2p_y} - 0.50\phi_{2s}] \quad (25.8)$$

$$\psi_b = N[0.61\phi_{2p_z} - 0.79\phi_{2p_y} - 0.50\phi_{2s}]$$

EXAMPLE PROBLEM 25.5

Normalize the hybrid orbitals given in Equation (25.8).

Solution

$$\begin{aligned} \int \psi_a^* \psi_a d\tau &= N^2 (0.61)^2 \int \phi_{2p_z}^* \phi_{2p_z} d\tau \\ &+ N^2 (0.79)^2 \int \phi_{2p_y}^* \phi_{2p_y} d\tau + N^2 (0.50)^2 \int \phi_{2s}^* \phi_{2s} d\tau = 1 \end{aligned}$$

Other terms do not contribute because the atomic orbitals are orthogonal to one another.

$$\int \psi_a^* \psi_a d\tau = N^2 (0.61)^2 + N^2 (0.79)^2 + N^2 (0.50)^2 = 1.25N^2 = 1$$

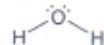
$$N = 0.89$$

Using the result of Example Problem 25.5, the normalized hybrid orbitals can be written as follows:

$$\begin{aligned}\psi_a &= 0.55\phi_{2p_z} + 0.71\phi_{2p_y} - 0.45\phi_{2s} \\ \psi_b &= 0.55\phi_{2p_z} - 0.71\phi_{2p_y} - 0.45\phi_{2s}\end{aligned}\quad (25.9)$$

Because the sum of the squares of the coefficients for each hybrid orbital equals one, we can calculate their *p* and *s* character. The fraction of *2p* character is $(0.55)^2 + (0.71)^2 = 0.80$. The fraction of *2s* character is $(-0.45)^2 = 0.20$. Therefore, the hybridization of the bonding hybrid orbitals is described as *sp*⁴. This differs from the first approximation *sp*³, as predicted by Bent's rule.

The two hybrid orbitals are shown in Figure 25.5. Note that each of the directed hybrid orbitals lies along one of the bonding directions and has little amplitude along the other bonding direction. These hybrid orbitals could be viewed as the basis for the line connecting bonded atoms in the Lewis structure for water



This figure shows a realistic representation of the hybrid orbitals that you should compare with the "slimmed down" version of Figure 25.3.

We now turn our attention to the lone pair electrons. The goal is to derive two additional mutually orthogonal hybrid orbitals for the lone pairs, each of which is orthogonal to σ_a and σ_b . Recall that the reason for making all lone pair and bonding orbitals orthogonal to one another is to create a local bonding model. If all the lone pair and bonding hybrids are orthogonal, they contribute independently to the electron density and the total energy to the maximum extent possible.

In constructing the hybrid lone pair orbitals, ϕ_{2p_z} is included. We again use the condition that if the coefficient of any one atomic orbital (which is given the index *j*) in the *i*th hybrid orbital is c_{ij}^l , then the sum of the square of the coefficients over all the hybrid orbitals is $\sum_i (c_{ij}^l)^2 = 1$. This condition ensures that no more total *s* and *p* character is distributed to the hybrid orbitals than the AO can provide. The steps in constructing the lone pair orbitals are described in Example Problem 25.6.

EXAMPLE PROBLEM 25.6

Derive the hybrid orbitals for the lone pairs on H₂O. To maximize the angular separation of the bonding and lone pair hybrids, choose the lone pair orbitals to be symmetric with respect to the *y*-*z* plane and to lie in a plane perpendicular to the plane of the bonding orbitals.

Solution

The lone pair orbitals have the form

$$\begin{aligned}\psi_c &= d_1\phi_{2p_z} + d_2\phi_{2p_y} + d_3\phi_{2s} + d_4\phi_{2p_x} \\ \psi_d &= d_5\phi_{2p_z} + d_6\phi_{2p_y} + d_7\phi_{2s} + d_8\phi_{2p_x}\end{aligned}$$

The calculation of the coefficients can be simplified by using the following symmetry arguments. Because the lone pair orbitals lie in the *x*-*z* plane, we know that the coefficient of ϕ_{2p_x} is zero. Because the *2s* orbital is spherically symmetrical,

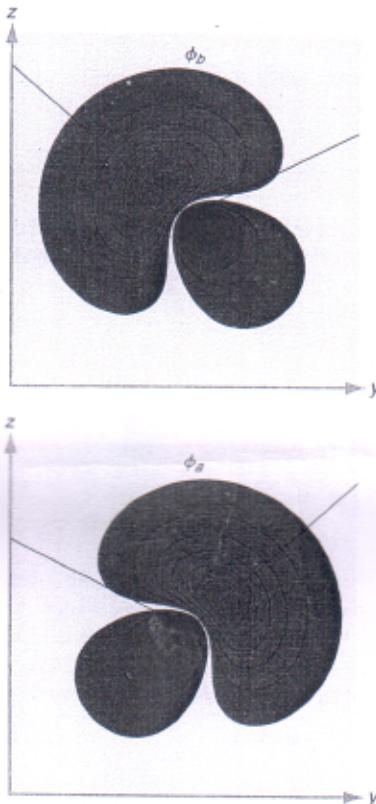


FIGURE 25.5
Directed hybrid bonding orbitals for H₂O. The black lines show the bond angle and orbital orientation. Red and blue contours correspond to the most positive and least positive values of the amplitude.

the coefficient of ϕ_{2s} is the same in both hybrids. Because the lone pair orbitals lie symmetrically above and below the $y-z$ plane, the coefficient of ϕ_{2p_z} is the same in both hybrids, and the coefficient of ϕ_{2p_x} in the two lone pair orbitals is equal in magnitude and opposite in sign. These conditions reduce the number of coefficients to three:

$$\psi_c = d_1 \phi_{2p_z} + d_3 \phi_{2s} + d_4 \phi_{2p_x}$$

$$\psi_d = d_1 \phi_{2p_z} + d_3 \phi_{2s} - d_4 \phi_{2p_x}$$

We now apply the condition $\sum_i (d_{ji})^2 + (c_{ji})^2 = 1$ to determine these three coefficients, using the known values c_i^j for the bonding hybrids:

$$d_1^2 + d_1^2 + (0.55)^2 + (0.55)^2 = 1 \quad \text{or} \quad d_1 = \sqrt{\frac{1-2\times(0.55)^2}{2}} = \pm 0.45$$

$$d_3^2 + d_3^2 + (0.45)^2 + (0.45)^2 = 1 \quad \text{or} \quad d_3 = \sqrt{\frac{1-2\times(0.45)^2}{2}} = \pm 0.55$$

$$d_4^2 + d_4^2 + (0)^2 + (0)^2 = 1 \quad \text{or} \quad d_4 = \sqrt{\frac{1-2\times(0)^2}{2}} = \pm 0.71$$

Which sign should be chosen for each of the coefficients? Coefficient d_1 is chosen to be negative so that the hybrid orbits for the lone pairs point in the $-z$ direction (away from the bonding hybrids). Coefficient d_3 is chosen to be negative for the reasons given above. Coefficient d_4 is chosen to be positive to make the lone pair hybrids orthogonal to the bonding hybrids. The resulting normalized lone pair orbitals that have the desired directional properties and are orthogonal to one another, as well as to the orbitals ψ_a and ψ_b , are given by

$$\psi_c = -0.45 \phi_{2p_z} - 0.55 \phi_{2s} + 0.71 \phi_{2p_x}$$

$$\psi_d = -0.45 \phi_{2p_z} - 0.55 \phi_{2s} - 0.71 \phi_{2p_x}$$

The hybrid orbital ψ_c points in the positive x direction and ψ_d points in the negative x direction. The general shape of these wave functions is similar, but not identical, to those shown in Figure 25.4.

The s character of the lone pair hybrids is $(0.55)^2 = 0.30$, and the p character is $(0.45)^2 + (0.71)^2 = 0.71$, for a hybridization of $sp^{2.3}$. In keeping with Bent's rule, the hybridization of the bonding hybrids has more p character than sp^3 , whereas the hybridization of the nonbonding electron pairs has more s character than sp^3 .

This calculation for H_2O illustrates how to construct bonding hybrid orbitals with a desired relative orientation. To this point, the energetics of this process have not been discussed. In many-electron atoms, the $2p$ orbital energy is greater than that for the $2s$ orbital. How can these orbitals be mixed in all possible proportions without putting energy into the atom? To create the set of occupied hybrid orbitals on an isolated ground-state oxygen atom would indeed require energy; however, the subsequent formation of bonds to the central atom lowers the energy, leading to an overall decrease in the energy of the molecule relative to the isolated atoms after bond formation. In the language of the hybridization model, the energy cost of promoting the electrons from the $1s^2 2s^2 2p^4$ configuration to the $1s^2 \psi_c^2 \psi_d^2 \psi_a^1 \psi_b^1$ configuration is more than offset by the energy gained in forming two O—H bonds.

Keep in mind that the individual steps in the formation of the H_2O molecule such as promotion of the O atom, followed by the creation of O—H bonds, are only an aid in describing the formation of H_2O , rather than a series of actual events. Ultimately, H_2O has a bond angle of 104.5° because this arrangement of the nuclei and the associated electrons minimizes the total energy of the molecule. The language of the hybridization model should not be taken too literally because neither the promotion