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LECTURE 22/36

OCT - 29 - 02

POLYATOMIC MOLECULES

READ TODAY'S LEC GRAY CH4 p116 - 135

NEXT LEC GRAY CH4 p135 - 144

FROM LAST LECTURE

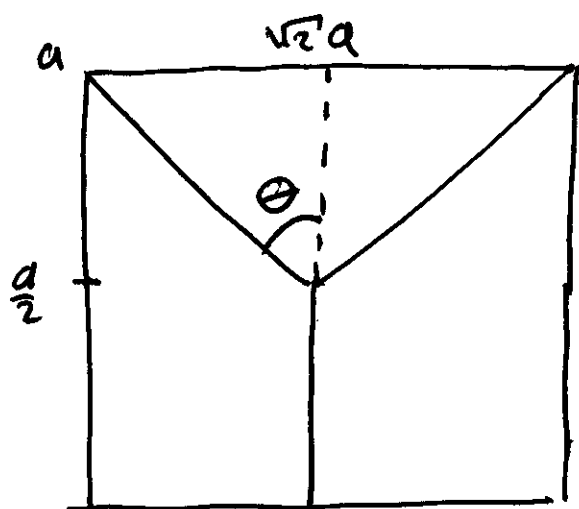
WE CONSIDER HYBRIDIZATION

B
sp

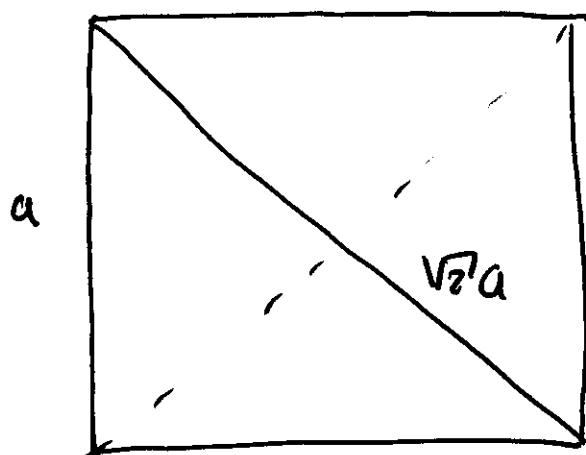
B
sp²

C
sp³

IN THE CASE OF sp³ WE HAVE
FOUR AO DIRECTED TOWARD THE
CORNERS OF A REGULAR TETRAHEDRON



CUT ALONG THE DIAGONAL



a
TOP VIEW

$$\tan \theta = \frac{\frac{\sqrt{2}a}{2}}{\frac{a}{2}} = \sqrt{2}$$

$$\theta = 54.735^\circ$$

$$2\theta = 109.47^\circ$$

9-20 sp^3 Hybrid Orbitals Are Directed Toward the Vertices of a Regular Tetrahedron

As our final example of the construction of hybrid orbitals, let us consider methane, CH_4 . The four C—H bonds in methane are equivalent and are directed toward the vertices of a regular tetrahedron. In the case of CH_4 , the molecular bond orbitals corresponding to Eq. 9-114 are

$$\begin{aligned}\phi_1 &= c_1 1s_A + d_1 \xi_1 \\ \phi_2 &= c_2 1s_B + d_2 \xi_2 \\ \phi_3 &= c_3 1s_C + d_3 \xi_3 \\ \phi_4 &= c_4 1s_D + d_4 \xi_4\end{aligned}\tag{9-130}$$

Following Eq. 9-113, we can write the hybrid orbitals on the carbon atom in methane as

$$\begin{aligned}\xi_1 &= a_1 2s_C + b_1 2p_{xC} + c_1 2p_{yC} + d_1 2p_{zC} \\ \xi_2 &= a_2 2s_C + b_2 2p_{xC} + c_2 2p_{yC} + d_2 2p_{zC} \\ \xi_3 &= a_3 2s_C + b_3 2p_{xC} + c_3 2p_{yC} + d_3 2p_{zC} \\ \xi_4 &= a_4 2s_C + b_4 2p_{xC} + c_4 2p_{yC} + d_4 2p_{zC}\end{aligned}\tag{9-131}$$

Because these hybrid orbitals are formed from one $2s$ orbital and three $2p$ orbitals, they are called sp^3 hybrid orbitals. By requiring these four hybrid orbitals to be equivalent, we have that $a_1 = a_2 = a_3 = a_4$. Using the condition $a_1^2 + a_2^2 + a_3^2 + a_4^2 = 1$, we find that $a_1 = a_2 = a_3 = a_4 = 1/\sqrt{4}$. Without loss of generality, we take one of the C—H bonds to be directed along the positive z axis. Because the $2p_x$ and $2p_y$ orbitals are directed along only the x and y axes, respectively, then b_1 and c_1 are zero in one of Eq. 9-131. If we let this orbital be ξ_1 , then

$$\xi_1 = \frac{1}{\sqrt{4}} 2s + d_1 2p_z$$

By requiring that ξ_1 be normalized, we have that

$$\frac{1}{4} + d_1^2 = 1$$

or that $d_1 = \sqrt{\frac{3}{4}}$. Therefore, ξ_1 becomes

$$\xi_1 = \frac{1}{\sqrt{4}} 2s + \sqrt{\frac{3}{4}} 2p_z\tag{9-132}$$

Equation 9-132 is the first of the four sp^3 hybrid orbitals that describe the bonding in methane. An electron-density contour map of an sp^3 orbital is shown in Figure 9-24.

Without any loss of generality, we take the second hybrid orbital to lie in the x - z plane, so that

$$\xi_2 = \frac{1}{\sqrt{4}} 2s + b_2 2p_x + d_2 2p_z\tag{9-133}$$

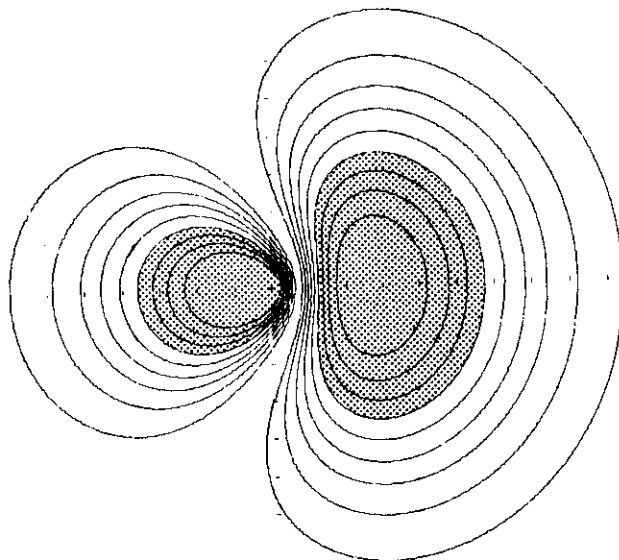


Figure 9-24. An electron-density contour map of an sp^3 hybrid orbital. [From G. Gerhold et al., *Am. J. Phys.* 40, 988 (1972).]

If we require ξ_2 to be orthogonal to ξ_1 , then we find

$$\frac{1}{4} + d_2\sqrt{\frac{3}{4}} = 0$$

or that $d_2 = -1/\sqrt{12}$. Equation 9-133 for ξ_2 now is

$$\xi_2 = \frac{1}{\sqrt{4}} 2s + b_2 2p_x - \frac{1}{\sqrt{12}} 2p_z$$

Now if we require that ξ_2 be normalized, then we have

$$\frac{1}{4} + b_2^2 + \frac{1}{12} = 1$$

or that $b_2 = \sqrt{2/3}$. Thus, the second sp^3 orbital is

$$\xi_2 = \frac{1}{\sqrt{4}} 2s + \sqrt{\frac{2}{3}} 2p_x - \frac{1}{\sqrt{12}} 2p_z \quad (9-134)$$

We can determine the direction in which ξ_2 points by differentiating ξ_2 with respect to θ . Using Eqs. 9-115 and 9-123 for the Slater orbitals in Eq. 9-134, we have (with $\phi = 0$)

$$\xi_2 = \frac{R(r)}{\sqrt{4\pi}} \left(\frac{1}{\sqrt{4}} + \sqrt{2} \sin \theta - \frac{\sqrt{3}}{\sqrt{12}} \cos \theta \right)$$

and so

$$\frac{d\xi_2}{d\theta} = 0 = \sqrt{2} \cos \theta + \frac{\sqrt{3}}{\sqrt{12}} \sin \theta$$

or that

$$\tan \theta = -\sqrt{8} \quad (9-135)$$

The value of θ given by Eq. 9-135 is $\theta = 109^\circ 28'$, the well-known tetrahedral

4/22

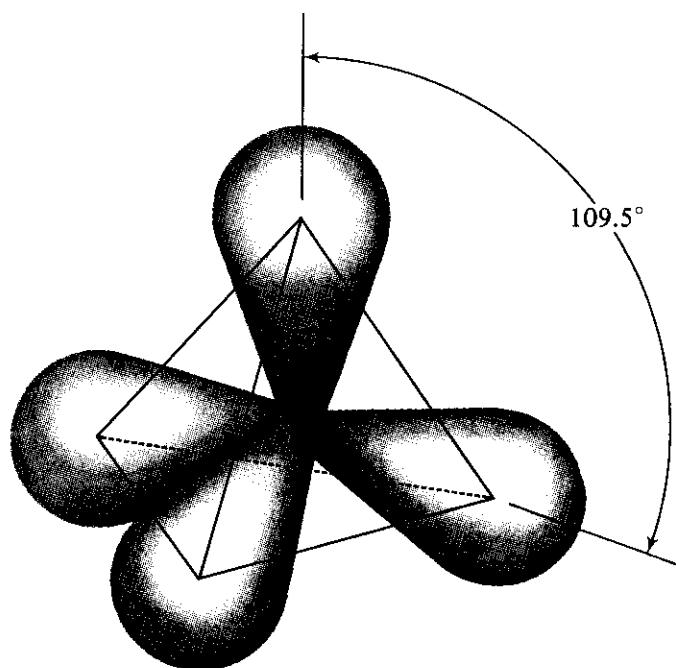


Figure 9-25. The geometry associated with sp^3 orbitals. The four sp^3 orbitals point toward the vertices of a tetrahedron. The angle between sp^3 orbitals is the tetrahedral bond angle 109.5° .

bond angle in methane. If we go on to determine ξ_3 and ξ_4 , then we shall find that ξ_1 , ξ_2 , ξ_3 , and ξ_4 are directed toward the vertices of a regular tetrahedron as shown in Figure 9-25. The methane molecule is described by overlapping a hydrogen $1s$ orbital with each of the sp^3 hybrid orbitals as shown in Figure 9-26. The electron configuration of methane in this localized orbital picture is $K(\phi_1)^2(\phi_2)^2(\phi_3)^2(\phi_4)^2$, where the ϕ 's are the four localized bond orbitals in Eq. 9-121.

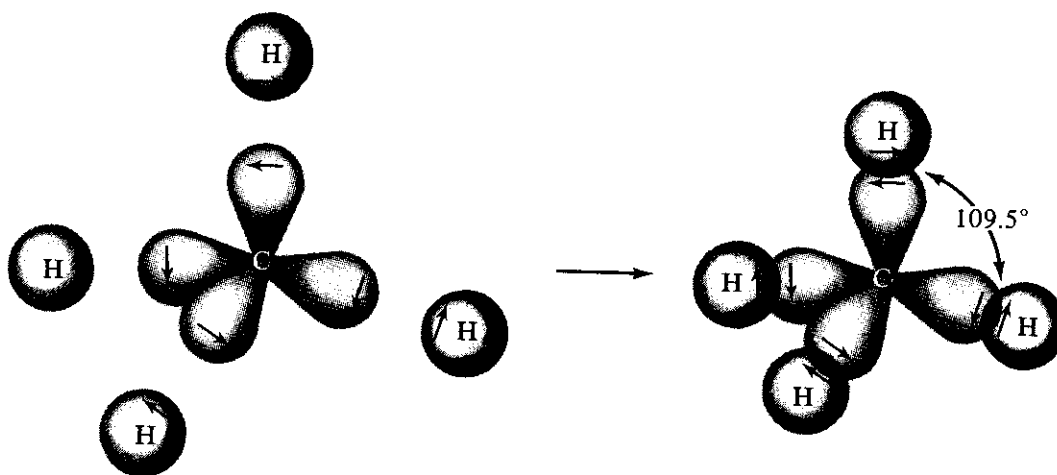


Figure 9-26. An illustration of the formation of four equivalent localized bond orbitals in CH_4 by overlapping the four carbon sp^3 orbitals and the hydrogen $1s$ orbitals. The eight valence electrons in CH_4 (four from the carbon atom and one from each hydrogen atom) occupy the four bond orbitals, accounting for the four localized carbon-hydrogen bonds in CH_4 .

EXAMPLE 9-10

A symmetric way of writing the four sp^3 hybrid orbitals is

$$\xi_1 = \frac{1}{\sqrt{4}}(2s + 2p_x + 2p_y + 2p_z)$$

$$\xi_2 = \frac{1}{\sqrt{4}}(2s - 2p_x - 2p_y + 2p_z)$$

$$\xi_3 = \frac{1}{\sqrt{4}}(2s + 2p_x - 2p_y - 2p_z)$$

$$\xi_4 = \frac{1}{\sqrt{4}}(2s - 2p_x + 2p_y - 2p_z)$$

Show that each of these hybrid orbitals is normalized and that they are mutually orthogonal.

Solution: The $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals are normalized and mutually orthogonal. Consequently,

$$\int \xi_1^2 d\tau = \frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} = 1$$

Because the coefficients in the other three hybrid orbitals are ± 1 , they are also normalized. The orthogonality condition is obtained by making an analogy of the ξ with vectors and forming the dot product. For example,

$$\int \xi_1 \xi_2 d\tau = \frac{1}{4}(1 - 1 - 1 + 1) = 0$$

Similarly,

$$\int \xi_1 \xi_3 d\tau = \frac{1}{4}(1 + 1 - 1 - 1) = 0$$

and so on.

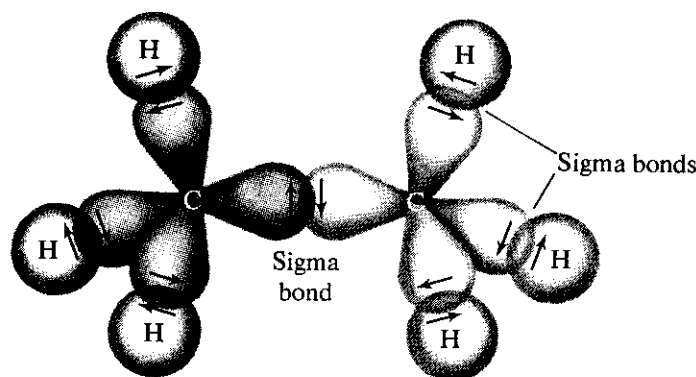
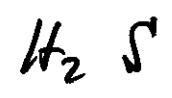
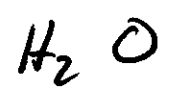
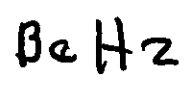
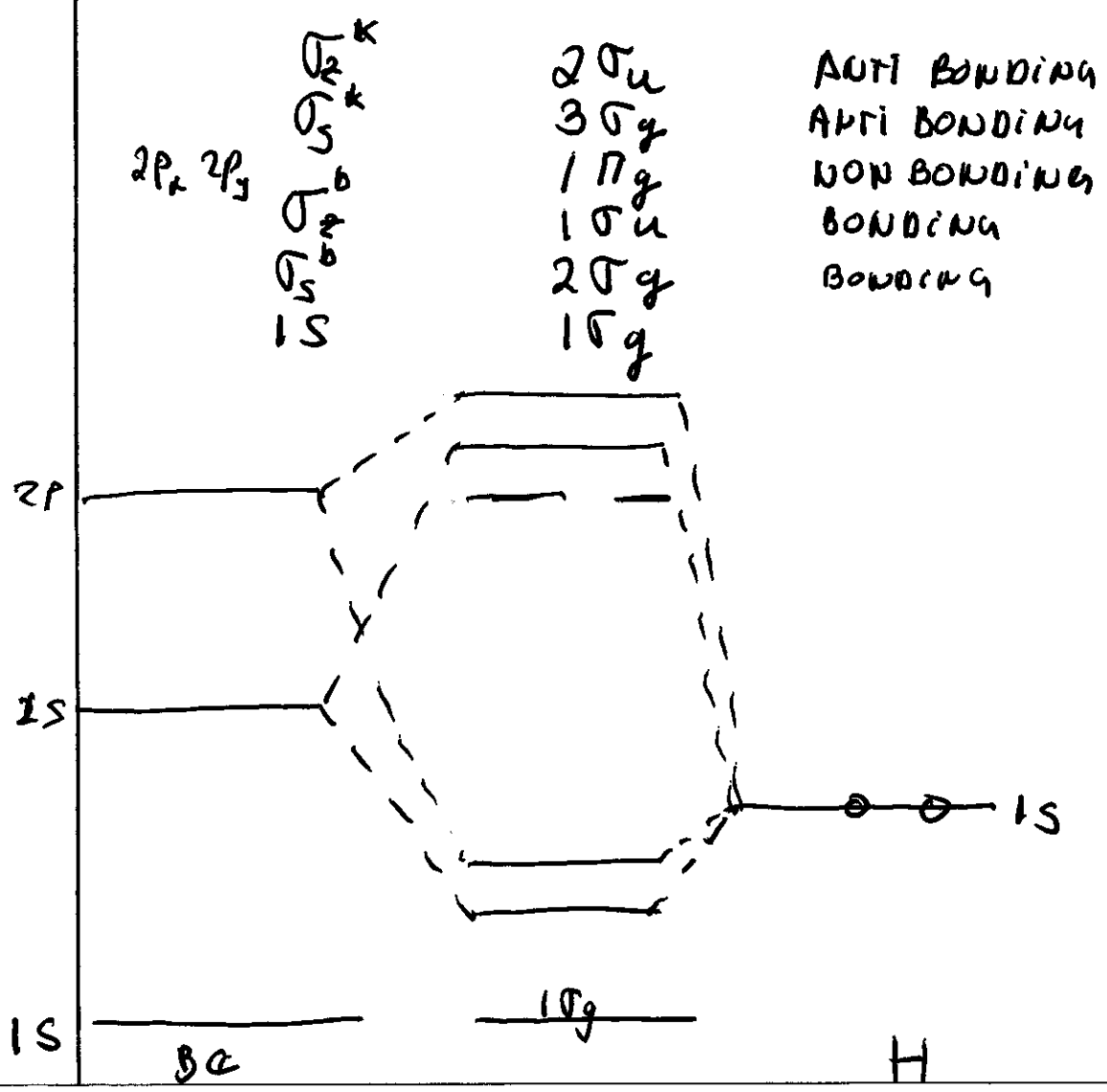


Figure 9-27. A schematic representation of the bonding in ethane, CH_3CH_3 . The seven bond orbitals in ethane result from the overlap of sp^3 orbitals on the carbon atoms and $1s$ orbitals on the hydrogen atoms. There are 14 valence electrons in ethane. Each of the seven bond orbitals is occupied by 2 valence electrons of opposite spins, accounting for the seven bonds in ethane. The electrons are depicted by arrows in the above figure.

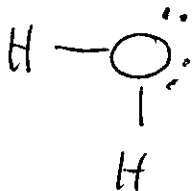
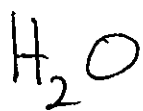
NOW WE ARE GOING TO LOOK BACK TO TRIATOMIC MOLECULES



FOR THE LINEAR BeH_2 MOLECULE WE FOUND THE FOLLOWING MO ORBITALS



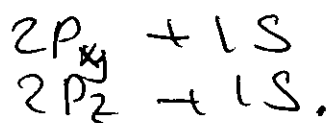
7/22



FROM O WE HAVE 6 e⁻s $(2s)^2(2p)^4$, SO WE CAN PLACE 4 e⁻s (LONE PAIRS) IN 2 sp^3 ORBITALS, AND USE THE OTHER 2 sp^3 ORBITALS TO BIND THE 2 H.

$$\text{H}-\text{O}-\text{H} \text{ ANGLE} = 109.5^\circ$$

IN THE DELOCALIZED MO METHOD, WE PLACE THE LONE PAIRS IN THE 2S AND ONE 2P ORBITALS, $(2s)^2(2p_x)^2$. FOR BINDING WE CONSIDER THE OTHER 2 2P ORBITALS



IN THIS CASE $\text{H}-\text{O}-\text{H}$ ANGLE = 90°

EXPERIMENTAL $\text{H}-\text{O}-\text{H}$ 105°

$$R_{\text{OH}} = 0.958 \text{ \AA}$$

8/22

BUT WE CONSIDER

$$\psi = c_1 2s + c_2 2p_x + c_3 2p_z$$

(sp^2 ORBITALS)

NOW WE HAVE 3 sp^2 AO AND $2p_y$.

TWO OF THE sp^2 ARE USED FOR BONDING
AND ONE FOR A LONE PAIR AS WELL AS $2p_y$.

FINALLY LCAO-MO

$$\psi = c_1 1s_{Ha} + c_2 1s_{Hb} + c_3 2s_A + c_4 2p_{xA} \\ + c_5 2p_{yA} + c_6 2p_{zA}$$

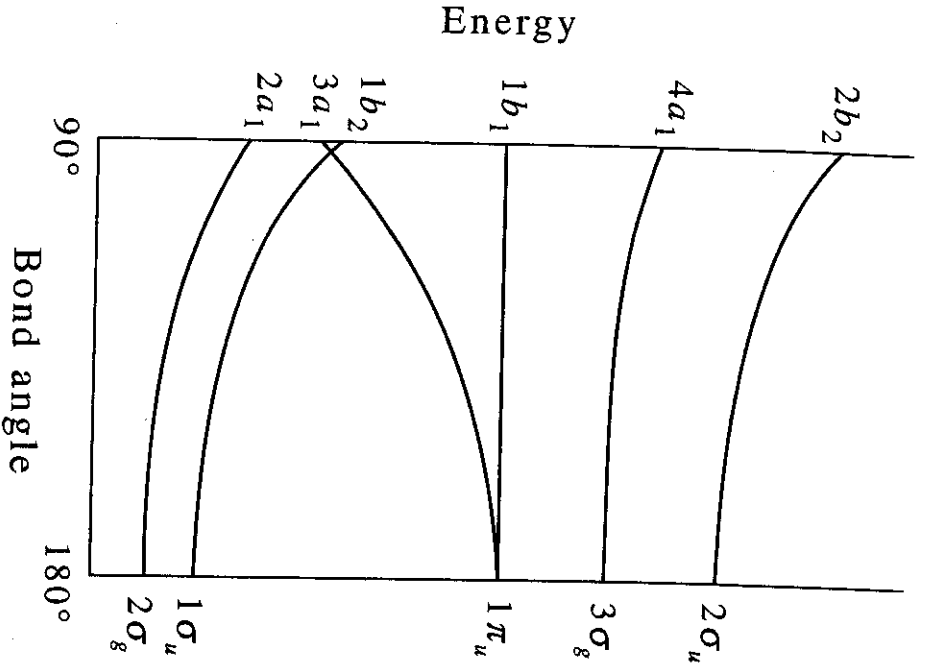


FIGURE 10.12

The Walsh correlation diagram for the valence electrons of an AH₂ molecule. The right side of the diagram gives the energy ordering of the molecular orbitals for an H-A-H bond angle of 180°. The left side gives the energy ordering of the molecular orbitals for an H-A-H bond angle of 90°. The solid lines tell us how the energies of the molecular orbitals depend upon H-A-H bond angles between 90° and 180°.

For a linear structure, this would correspond to the electron configuration of $(2\sigma_g)^2(1\sigma_u)^2$. A bent structure would have an electron configuration of $(2a_1)^2(1b_2)^2$ or $(2a_1)^2(3a_1)^2$, depending on the bond angle. Because bending destabilizes the energy of the lowest two molecular orbitals, the electron configuration $(2\sigma_g)^2(1\sigma_u)^2$ is lower in energy than either $(2a_1)^2(1b_2)^2$ or $(2a_1)^2(3a_1)^2$.

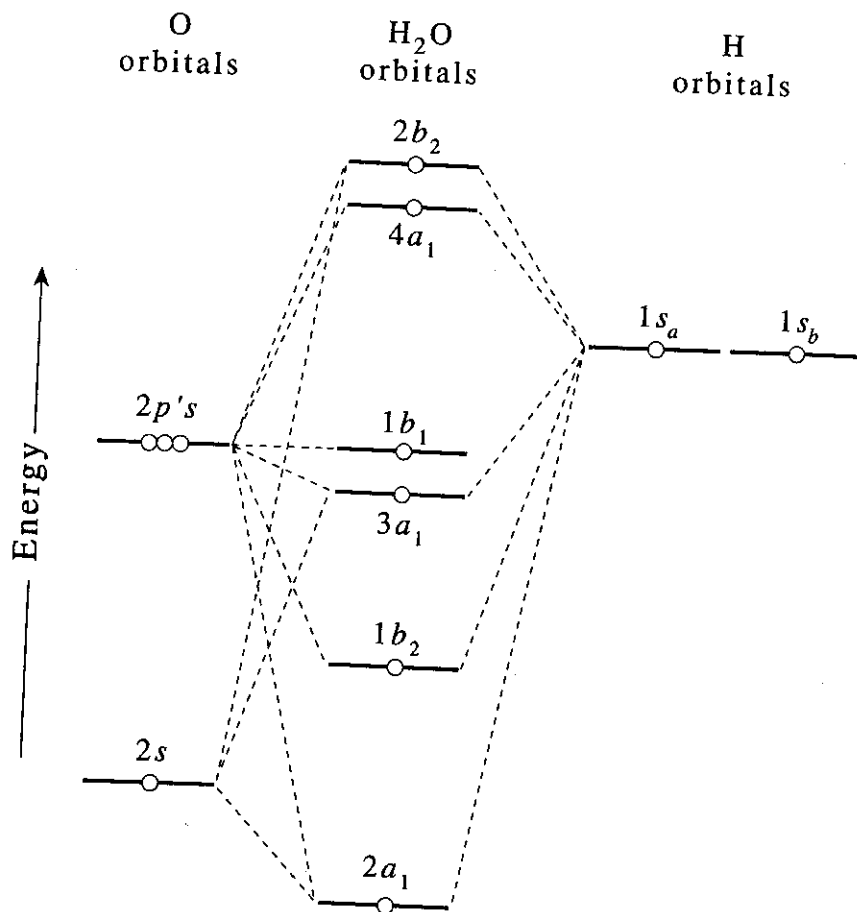


FIGURE 10.13
 A molecular-orbital energy-level diagram for the valence electrons in H₂O. (The bond angle is 104.5°, the equilibrium value.) Note that the 1b₁ orbital is a nonbonding orbital.

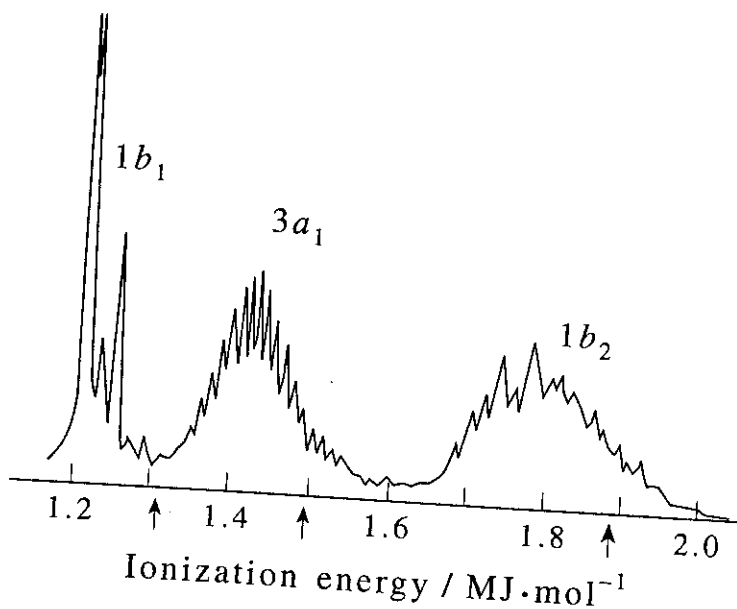
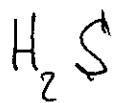


FIGURE 10.14
 The photoelectron spectrum of water. The three bands shown correspond to ionization from the three highest energy occupied molecular orbitals. The fine structure on each band reflects ionization to different vibrational levels. The arrows indicate the calculated ionization energies from the $\nu = 0$ vibrational states (see Chapter 11).

1/22



FOR THIS MOLECULE WE FIND THAT THE
EXPERIMENTAL ANGLE H-S-H IS
 92° \Rightarrow sp ORBITALS

AS THE CENTRAL ATOM BECOMES LARGER
THE VALENCE e⁻'S ARE FARTHER FROM EACH OTHER

12/22

VALENCE-SHELL ELECTRON-PAIR REPULSION (VSEPR)

LOCALIZED MO sp , sp^2 , sp^3 , sp^3d , sp^3d^2

MINIMIZE
REPULSIONS

lone-lone PAIRS

lone-bonded PAIRS

bonded-bonded PAIRS

BONDING σ ARE PULLED TOWARD; THE MORE

ELECTRONEGATIVE ATOM \Rightarrow BOND DIPOLE

BOND DIPOLES HAVE TO SUM AS VECTORS

H_2O POLAR

CCl_4 NON POLAR