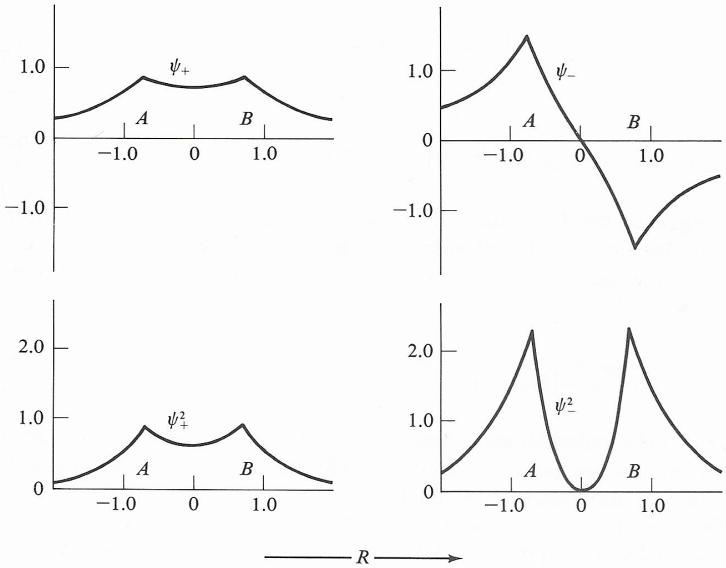

Figure 9-7. The molecular orbitals ψ_+ and ψ_- from Eq. 9-69 and their squares plotted along the internuclear axis.

(e.g., the hydrogenlike atomic orbitals), whereas in the molecular case we have only two H_2^+ molecular orbitals. It is important to realize that we obtained only two molecular orbitals because we used a linear combination of only two atomic orbitals as our trial function (Eq. 9-52). This was done solely for simplicity, and one could have just as well used a linear combination such as

$$\psi = c_1 1s_A + c_2 2s_A + c_3 2p_{zA} + c_4 1s_B + c_5 2s_B + c_6 2p_{zB} \tag{9-72}$$

This particular choice would lead to a 6 × 6 secular determinant with six energies and six molecular orbitals instead of just two. Clearly there is no limit to this procedure and we could generate a large set of molecular orbitals. For pedagogical reasons, however, we shall develop a molecular-orbital theory of H_2 using just Eq. 9-70 and 9-71.

9-7 *The Simple Valence-Bond Theory Ignores Ionic Terms and the Simple Molecular-Orbital Theory Overemphasizes Ionic Terms*

Because ψ_b is the molecular orbital corresponding to the ground-state energy, we can describe the ground state of H_2 by placing two electrons with opposite spins in ψ_b. The Slater determinant corresponding to this assignment is

$$\psi = \frac{1}{\sqrt{2!}}\begin{vmatrix} \psi_b\alpha(1) & \psi_b\beta(1) \\ \psi_b\alpha(2) & \psi_b\beta(2) \end{vmatrix} \tag{9-73}$$

$$= \psi_b(1)\psi_b(2)\left[\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]\right] \tag{9-74}$$

Once again we see the spatial and spin separation that occurs for a two-electron system. Because the Hamiltonian is taken to be independent of spin, we can calculate the energy using only the spatial part of Eq. 9-74. Using Eq. 9-70 for ψ_b, we find

$$\psi_{\text{MO}} = \frac{1}{[2(1+S)]}[1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)] \tag{9-75}$$

Note that the molecular wave function here is a product of molecular orbitals, which in turn are linear combinations of atomic orbitals. This method of constructing molecular wave functions is known as the *LCAO-MO* (*linear combination of atomic orbitals-molecular orbital*) method and has been successfully extended and applied to a variety of molecules as we shall see in Section 9-16.

If we substitute the normalized LCAO-MO wave function, Eq. 9-75, into

$$E = \int \psi \hat{H} \psi \, d\mathbf{r}_1 \, d\mathbf{r}_2 \tag{9-76}$$

to find $E_{\text{MO}}(R)$, then the resulting integrals are similar to those that we encountered in the Heitler-London valence-bond method. The integrals can be evaluated analytically, but they result in functions that are somewhat advanced. If $E_{\text{MO}}(R)$ is plotted versus R, then one finds $E_{\text{dissociation}} = 0.099$ au $= 2.70$ eV, $R_{\text{min}} = 1.61$ au $= 0.085$ nm, and a fundamental vibrational frequency $\bar{\nu} = 4.16 \times 10^3$ cm^{-1}. The experimental values of these quantities are given in Table 9-1 along with the results obtained from Eq. 9-75 when the orbital exponent in the 1*s* orbital is allowed to vary.

The valence-bond method and the molecular-orbital method may appear to be two rather different approaches to chemical bonding or to H_2 in particular. Although the two methods appear to be quite different and in a sense competitive, they actually are closely related to each other. To see their relation, consider the (unnormalized) molecular-orbital wave function

$$\begin{aligned}\psi_{\text{MO}} &= [1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)] \\ &= 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2) + 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)\end{aligned} \tag{9-77}$$

The first two terms here are just ψ_{VB}, our valence-bond wave function for H_2. What do the second two terms correspond to? These terms represent the electron configurations in which both electrons are on one atom. We can describe these two terms by the electron-dot formulas

$$\mathrm{H}_A\!:\quad \mathrm{H}_B \quad \text{and} \quad \mathrm{H}_A \quad :\!\mathrm{H}_B$$

or as

$$\mathrm{H}_A^-\,\mathrm{H}_B^+ \quad \text{and} \quad \mathrm{H}_A^+\,\mathrm{H}_B^-$$

Thus, we see that third and fourth terms in Eq. 9-77 represent ionic structures for H_2.

If we let

$$\psi_{\text{ionic}} = 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) \tag{9-78}$$

then we can write Eq. 9-77 as

$$\psi_{\text{MO}} = \psi_{\text{VB}} + \psi_{\text{ionic}} \tag{9-79}$$

Equation 9-79 suggests that ψ_{MO} overemphasizes ionic terms, whereas ψ_{VB} underemphasizes (ignores) them.

We can develop a method intermediate to the VB and MO methods by using a linear combination of the form

$$\psi = c_1\psi_{\text{VB}} + c_2\psi_{\text{ionic}} \tag{9-80}$$

This was done by Weinbaum in 1933, who found $R_{\text{min}} = 1.67$ au $= 0.088$ nm and $E_{\text{dissociation}} = 0.1187$ au $= 3.23$ eV with $Z = 1$, and $R_{\text{min}} = 1.43$ au $=$ 0.076 nm and $E_{\text{dissociation}} = 0.1478$ au $= 4.03$ eV when Z was allowed to vary. In addition, Weinbaum found that $c_2/c_1 = 0.16$ at R_{min} for the $Z = 1$ case. Some people would say that this implies that there is 0.16 or really $(0.16)^2 = 0.03$ ionic character in H_2, but this is a shaky interpretation. For instance, Weinbaum also found that $c_2/c_1 = 0.26$ for the optimum value of Z, and so we see that the ratio depends on the functions used in ψ_{VB} and ψ_{ionic}. In fact, as we have discussed briefly earlier, one does not need to use simple $1s$ orbitals. For example, it is clear that the electron distributions in each hydrogen atom do not remain spherical as the two atoms approach each other. If we let the internuclear axis be the z axis, then we might try constructing our valence-bond orbitals out of a linear combination of a $1s$ orbital and a $2p_z$ orbital

$$\phi = 1s + \lambda 2p_z \tag{9-81}$$

instead of from just a $1s$ orbital. In this case, we would have

$$\psi_{\text{VB}} = \phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2) \tag{9-82}$$

where ϕ_A and ϕ_B are given by Eq. 9-81. Equation 9-82 was used by Rosen in 1931 (see Table 9-1), and ionic terms were included 2 years later by Weinbaum (see Table 9-1). If this procedure is carried to its extreme, then we include more and more terms in Eq. 9-81 and will eventually reach the Hartree-Fock limit like we did in the atomic case. We shall discuss the Hartree-Fock method for molecules in Section 9-16.

9-8 *Valence-Bond Theory Plus Ionic Terms Are Formally Identical to Molecular-Orbital Theory with Configuration Interaction*

The relation between the valence-bond theory and molecular-orbital theory is even more complete than we have shown up to now. Consider our simple LCAO treatment of H_2^+, in which we obtained the (unnormalized) molecular orbitals

$$\begin{aligned}\phi_b &= 1s_A + 1s_B \\ \phi_a &= 1s_A - 1s_B\end{aligned} \tag{9-83}$$

In our molecular-orbital discussion, we used

$$\psi = \begin{vmatrix}\phi_b\alpha(1) & \phi_b\beta(1)\\ \phi_b\alpha(2) & \phi_b\beta(2)\end{vmatrix} \tag{9-84}$$

or simply its spatial part, $\phi_b(1)\phi_b(2)$. However, we can extend our molecular-orbital treatment by using the antibonding molecular orbital ϕ_a as well. Considering only spatial parts for simplicity, we can form

$$\begin{aligned}\psi_1 &= \phi_b(1)\phi_b(2)\\ \psi_2 &= \phi_b(1)\phi_a(2) + \phi_a(1)\phi_b(2)\\ \psi_3 &= \phi_b(1)\phi_a(2) - \phi_a(1)\phi_b(2)\\ \psi_4 &= \phi_a(1)\phi_a(2)\end{aligned} \tag{9-85}$$

We should take a linear combination of these four wave functions as a trial function and obtain a 4 × 4 determinant, but it is algebraically easier to start with ψ_1 and to add in each wave function in turn. Consider just ψ_1 and ψ_2 first. In this case, then

$$\psi = c_1\psi_1 + c_2\psi_2$$

and

$$\begin{vmatrix}H_{11} - ES_{11} & H_{12} - ES_{12}\\ H_{12} - ES_{12} & H_{22} - ES_{22}\end{vmatrix} = 0 \tag{9-86}$$

where

$$\begin{aligned}H_{12} &= \iint \psi_1 \hat{H} \psi_2 \, d\mathbf{r}_1 \, d\mathbf{r}_2\\ &= \iint \phi_b(1)\phi_b(2)\hat{H}[\phi_b(1)\phi_a(2) + \phi_a(1)\phi_b(2)]\, d\mathbf{r}_1\, d\mathbf{r}_2\end{aligned} \tag{9-87}$$

Consider now the integral

$$\begin{aligned}I &= \int \phi_b(2)\hat{H}\phi_a(2)\, d\mathbf{r}_2\\ &= \int [1s_A(2) + 1s_B(2)]\hat{H}[1s_A(2) - 1s_B(2)]\, d\mathbf{r}_2\end{aligned} \tag{9-88}$$

Note that this integral appears in H_{12} in Eq. 9-87. It is possible to show that I vanishes without doing any intergrations at all. We simply shall appeal to a symmetry argument. The subscripts A and B denote the labels of the two hydrogen nuclei. The Hamiltonian is symmetric in A and B, in the sense that it does not change if we relabel the two nuclei by replacing A by B and B by A. Thus, if we interchange A and B in Eq. 9-88, then we find that $I = -I$. The fact that $I = -I$ implies that $I = 0$ and eventually that $H_{12} = 0$ in Eq. 9-87. Similarly, it is straightforward to show that $S_{12} = 0$ (Problem 16), and so Eq. 9-86 becomes

$$\begin{vmatrix} H_{11} - E & 0 \\ 0 & H_{22} - E \end{vmatrix} = 0 \tag{9-89}$$

The two roots to Eq. 9-89 are simply H_{11} and H_{22}, which are the results that we would have obtained if we had used ψ_1 and ψ_2 separately. Thus, we see that the two states described by ψ_1 and ψ_2 have no influence on each other. We say that ψ_1 and ψ_2 do not interact or mix.

Now let us consider a linear combination of ψ_1 and ψ_3 in Eq. 9-85. By a similar analysis (Problem 17), we find that ψ_1 and ψ_3 do not interact or mix. The only wave function in Eq. 9-85 that interacts with ψ_1 is ψ_4.

EXAMPLE 9-4

Show that the symmetry argument that we used to show that ψ_1 does not mix with ψ_2 and ψ_3 does *not* imply that ψ_1 does not mix with ψ_4.

Solution: The integral of interest here is H_{14}, because if $H_{14} = 0$, then ψ_1 and ψ_4 do not mix, and if $H_{14} \neq 0$, then ψ_1 and ψ_4 do mix. The integral H_{14} is

$$H_{14} = \iint d\mathbf{r}_1\, d\mathbf{r}_2\, \phi_b(1)\phi_b(2)\hat{H}\phi_a(1)\phi_a(2)$$

The argument that we have used to show that H_{12} and H_{13} equal zero is based upon the fact that $\phi_a \to -\phi_a$ when nuclei A and B are interchanged. For example (see Eq. 9-87),

$$H_{12} = \iint d\mathbf{r}_1\, d\mathbf{r}_2\, \phi_b(1)\phi_b(2)\hat{H}\phi_b(1)\phi_a(2) + \iint d\mathbf{r}_1\, d\mathbf{r}_2\, \phi_b(1)\phi_b(2)\hat{H}\phi_a(1)\phi_b(2)$$

When the two nuclei are interchanged, ϕ_b and $\hat{H}$ remain unchanged, but $\phi_a \to -\phi_a$ in each of the two integrals in H_{12}. Thus, we find that $H_{12} = -H_{12}$, which implies that $H_{12} = 0$.

Note that H_{14}, however, contains two factors of ϕ_a, the two factors being $\phi_a(1)$ and $\phi_a(2)$. Thus, H_{14} does *not* change sign upon the interchange of the two nuclei. Consequently, we cannot conclude from a symmetry argument that H_{14} equals zero, and in fact H_{14} does not equal zero.

The linear combination

$$\begin{aligned} \psi_{\text{CI}} &= c_1\psi_1 + c_4\psi_4 \\ &= c_b\phi_b(1)\phi_b(2) + c_a\phi_a(1)\phi_a(2) \end{aligned} \tag{9-90}$$

describes the ground state of H_2. Equation 9-90 is a ground-state molecular-orbital wave function with an excited-state configuration mixed in. The extension of simple molecular-orbital theory to include excited-state configurations is called *configuration interaction.* The CI subscript in Eq. 9-90 denotes that ψ_{CI} is a configuration interaction wave function.

Let us look at ψ_{CI} given by Eq. 9-90 in more detail. Equation 9-90 can be written out as

$$\begin{aligned} \psi_{\text{CI}} &= c_b[1s_A(1)1s_A(2) + 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2) + 1s_B(1)1s_B(2)] \\ &\quad + c_a[1s_A(1)1s_A(2) - 1s_A(1)1s_B(2) - 1s_B(1)1s_A(2) + 1s_B(1)1s_B(2)] \\ &= (c_b - c_a)\psi_{\text{VB}} + (c_b + c_a)\psi_{\text{ionic}} \end{aligned} \tag{9-91}$$

Thus, we see that molecular-orbital theory with configuration interaction is exactly the same as valence-bond theory with ionic terms included. Both methods become exact in the limit of including more and more covalent and ionic terms or more and more excited-state configurations. In practice, however, one does not use the complete limit and so the two methods do differ. Each method has its advantages in certain applications, but molecular-orbital theory plus configuration interaction is much more widely used.

Before finishing our discussion of H_2, we should discuss briefly the early work of James and Coolidge (1933) and the more recent work of Kolos and Wolniewicz (1968). We saw in Chapter 8 that Hylleras was able to obtain essentially the exact ground-state energy of the helium atom by including the interelectronic distance r_{12} explicitly in the trial wave function. A similar approach was applied to H_2 with equal success by James and Coolidge as early as 1933.

When discussing the hydrogen molecule and evaluating the various integrals that occur, it is natural to use a coordinate system called *elliptic coordinates* (see also Problem 3). The three coordinates used to specify the location of a point in elliptic coordinates are

$$\lambda = \frac{r_A + r_B}{R_{AB}} \qquad \mu = \frac{r_A - r_B}{R_{AB}} \tag{9-92}$$

and ϕ, which is the angle of the (r_A, r_B, R_{AB}) triangle about the interfocal axis. For the two electrons in H_2 we have

$$\begin{aligned} \lambda_1 &= \frac{r_{1A} + r_{1B}}{R_{AB}} \qquad & \lambda_2 &= \frac{r_{2A} + r_{2B}}{R_{AB}} \\ \mu_1 &= \frac{r_{1A} - r_{1B}}{R_{AB}} \qquad & \mu_2 &= \frac{r_{2A} - r_{2B}}{R_{AB}} \end{aligned} \tag{9-93}$$

In addition to these four coordinates, James and Coolidge also introduced a fifth coordinate

$$\rho = \frac{r_{12}}{R_{AB}} \tag{9-94}$$

and used a spatially symmetric trial function of the form

$$\psi = e^{-\alpha(\lambda_1+\lambda_2)} \sum_{m,n,j,k,p} c_{mnjkp}(\lambda_1^m \lambda_2^n \mu_1^j \mu_2^k \rho^p + \lambda_1^n \lambda_2^m \mu_1^k \mu_2^j \rho^p) \tag{9-95}$$

where α and the c_{mnjkp}'s are variational parameters. Using 13 terms in this expansion, James and Coolidge found $E_{\text{dissociation}} = 0.1735$ au $= 4.72$ eV and $R_{\text{min}} = 1.40$ au $= 0.074$ nm, in excellent agreement with the experimental values (see Table 9-1). A more recent calculation by Kolos and Wolniewicz in 1968 gave a dissociation energy of 0.1745 au $=$ 4.75 eV, in complete agreement with experiment.

We can see in Table 9-1 that the dissociation energy and the equilibrium bond distance obtained by James and Coolidge or by Kolos and Wolniewicz are in excellent accord with the experiment values. The calculation of James and Coolidge represents one of the great early achievements of quantum mechanics as applied to chemistry.

9-9 *Molecular Orbitals Can Be Ordered According to Their Energies*

We can use either the valence-bond theory or the molecular-orbital theory to treat molecules that are more complicated than H_2. A great advantage of the molecular-orbital theory is that we can construct a set of molecular orbitals into which we can place electrons in accord with the Pauli Exclusion Principle. The assignment of electrons to molecular orbitals will allow us to introduce electron configurations for molecules just as we did for atoms in Chapter 8. To do this, we must construct sets of molecular orbitals. We shall construct molecular orbitals for homonuclear diatomic molecules in some detail and then just present some results for heteronuclear diatomic molecules and polyatomic molecules.

We shall use the LCAO-MO approximation, in which we form molecular orbitals as linear combinations of atomic orbitals. In the simplest case, we have only one atomic orbital centered on each atom and, as in the molecular-orbital treatment of H_2 discussed in Section 9-7, the two molecular orbitals are

$$\psi_{\pm} = 1s_A \pm 1s_B$$

if we start with a 1*s* orbital on each atom. These two molecular orbitals are shown in Figure 9-8. Note that ψ_+ concentrates electron density in the region