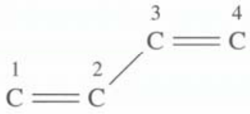
of atomic orbitals that act as bases for the various irreducible representations. This question is the topic of the next section.

12–9. Generating Operators Are Used to Find Linear Combinations of Atomic Orbitals That Are Bases for Irreducible Representations

There is a straightforward procedure to find linear combinations of atomic orbitals that are bases for the irreducible representations. It involves a quantity called a *generating operator*, whose formula we give without proof. The generating operator for the jth irreducible representation is

$$\hat{P}_j = \frac{d_j}{h}\sum_{\hat{R}} \chi_j(\hat{R})\hat{R} \tag{12.32}$$

Recall that d_j is the dimensionality of the jth irreducible representation. Equation 12.32 may look formidable, but it is really easy to use. Before we use it to generate symmetry orbitals for benzene, with its relatively large $\mathbf{D}_{6h}$ character table, let's use it to generate symmetry orbitals for butadiene. Recall that we applied Hückel molecular-orbital theory to butadiene in Section 10–6. The skeletal π-electron framework of butadiene



suggests that we use the $\mathbf{C}_{2h}$ point-group elements (Table 12.10). If we denote the $2p_z$ orbital an carbon atom i by ψ_i, Equation 12.32 gives

$$\begin{aligned}
\hat{P}_{A_g}\psi_1 &= \tfrac{1}{4}\textstyle\sum_{\hat{R}} \chi_{A_g}(\hat{R})\hat{R}\psi_1 \\
&= \tfrac{1}{4}[(1)\hat{E}\psi_1 + (1)\hat{C}_2\psi_1 + (1)\hat{\imath}\psi_1 + (1)\hat{\sigma}_h\psi_1] \\
&= \tfrac{1}{4}(\psi_1 + \psi_4 - \psi_4 - \psi_1) = 0 \\
\hat{P}_{A_g}\psi_2 &= \tfrac{1}{4}(\psi_2 + \psi_3 - \psi_3 - \psi_2) = 0
\end{aligned}$$

with similar results for ψ_3 and ψ_4. Similarly, using ψ_1 and ψ_2, we get

$$\begin{aligned}
\hat{P}_{B_g}\psi_1 &= \tfrac{1}{4}(\psi_1 - \psi_4 - \psi_4 + \psi_1) \propto \psi_1 - \psi_4 \\
\hat{P}_{B_g}\psi_2 &= \tfrac{1}{4}(\psi_2 - \psi_3 - \psi_3 + \psi_2) \propto \psi_2 - \psi_3 \\
\hat{P}_{A_u}\psi_1 &= \tfrac{1}{4}(\psi_1 + \psi_4 + \psi_4 + \psi_1) \propto \psi_1 + \psi_4 \\
\hat{P}_{A_u}\psi_2 &= \tfrac{1}{4}(\psi_2 + \psi_3 + \psi_3 + \psi_2) \propto \psi_2 + \psi_3 \\
\hat{P}_{B_u}\psi_1 &= \hat{P}_{B_u}\psi_2 = 0
\end{aligned} \tag{12.33}$$

We have ignored the numerical factors in front of the various symmetry orbitals because we are interested only in their functional form. Their subsequent normalization is a simple matter.

Equations 12.33 give us four symmetry orbitals, two belonging to B_g symmetry and two belonging to A_u symmetry. Using these symmetry orbitals, the Hückel molecular-orbital theory secular determinant of butadiene factors into two 2×2 blocks. The actual form is (Problem 12–28)

$$\left|\begin{array}{cc|cc} x & 1 & 0 & 0 \\ 1 & x+1 & 0 & 0 \\ \hdashline 0 & 0 & x & 1 \\ 0 & 0 & 1 & x-1 \end{array}\right| = 0$$

or

$$(x^2 + x - 1)(x^2 - x - 1) = 0 \tag{12.34}$$

or

$$x = \frac{-1 \pm \sqrt{5}}{2} \qquad \text{and} \qquad x = \frac{1 \pm \sqrt{5}}{2}$$

or $x = 0.6180,\ -1.6180,\ 1.6180$, and -0.6180. These are the very same values we obtained in Section 10–6, but there we had to deal with a quartic equation for x because the secular determinant was not in block diagonal form.

Note above that no symmetry orbitals belong to A_g or B_u. It turns out that we really did not have to apply the generating operators for A_g and B_u to learn this. Let's apply the four group operations to the four $2p_z$ orbitals in Figure 12.11. For the identity operation, $\hat{E}\psi_j = \psi_j$ for each j. We can write this result in matrix form:

$$\hat{E}\begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}$$

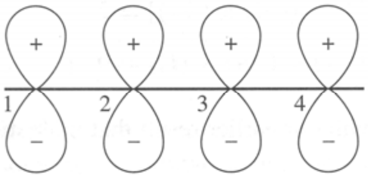


FIGURE 12.11
A schematic illustration of the four $2p_z$ orbitals used to form Hückel molecular orbitals for butadiene.