EXAMPLE 12–13

Suppose that $\Gamma = 3\ 0\ -1$ for $\mathbf{C}_{3v}$. Determine the a_i's in Equation 12.23.

SOLUTION: We use Equation 12.23 as a sum over classes, in which case we have

$$a_{A_1} = \frac{1}{6}[(1) \times (3) \times (1) + (2) \times (0) \times (1) + (3) \times (-1) \times (1)] = 0$$

$$a_{A_2} = \frac{1}{6}[(1) \times (3) \times (1) + (2) \times (0) \times (1) + (3) \times (-1) \times (-1)] = 1$$

$$a_E = \frac{1}{6}[(1) \times (3) \times (2) + (2) \times (0) \times (-1) + (3) \times (-1) \times (0)] = 1$$

or $\Gamma = A_2 + E$.

12–8. We Use Symmetry Arguments to Predict Which Elements in a Secular Determinant Equal Zero

Recall from Chapters 9 and 10 that we encountered molecular integrals of the type

$$H_{ij} = \int \phi_i^* \hat{H} \phi_j d\tau \quad \text{and} \quad S_{ij} = \int \phi_i^* \phi_j d\tau \tag{12.24}$$

We will now show that integrals like these will be equal to zero if we choose ϕ_i^* and ϕ_j such that they belong to different irreducible representations. For simplicity, we will prove this only for one-dimensional irreducible representations, but the result is general. Let's start with the overlap integral

$$S_{ij} = \int \phi_i^* \phi_j d\tau \tag{12.25}$$

This integral is just some number, and its value certainly cannot depend upon how we orient the molecule. A symmetry operation of the molecule $\hat{R}$ transforms ϕ_i and ϕ_j to $\hat{R}\phi_i$ and $\hat{R}\phi_j$, respectively. The resulting (transformed) overlap integral is

$$\hat{R}S_{ij} = \int \hat{R}\phi_i^* \hat{R}\phi_j d\tau$$

Because the value of S_{ij} cannot change when we apply a symmetry operation of the point group of the molecule

$$\hat{R}S_{ij} = \int \hat{R}\phi_i^* \hat{R}\phi_j d\tau = S_{ij} = \int \phi_i^* \phi_j d\tau \tag{12.26}$$

Suppose now that ϕ_i^* and ϕ_j are bases for the (one-dimensional) irreducible representations Γ_a and Γ_b. If that is so, then

$$\hat{R}\phi_i^* = \chi_a(\hat{R})\phi_i^* \quad \text{and} \quad \hat{R}\phi_j = \chi_b(\hat{R})\phi_j \tag{12.27}$$

In fact, Equations 12.27 are exactly what we mean when we say that ϕ_i^* and ϕ_j are bases for the one-dimensional irreducible representations Γ_a and Γ_b (see Example 12–9). If we substitute Equations 12.27 into Equation 12.26, we obtain

$$S_{ij} = \chi_a(\hat{R})\chi_b(\hat{R}) \int \phi_i^*\phi_j d\tau = \chi_a(\hat{R})\chi_b(\hat{R}) S_{ij} \tag{12.28}$$

Equation 12.28 requires that

$$\chi_a(\hat{R})\chi_b(\hat{R}) = 1 \qquad \text{for all } \hat{R} \tag{12.29}$$

Because $\chi_i(\hat{R})$ is either 1 or -1 for any one-dimensional irreducible representation, Equation 12.29 is true only if $\chi_a(\hat{R}) = \chi_b(\hat{R})$, or if Γ_a and Γ_b are the same irreducible representation. If $\chi_a(\hat{R}) \neq \chi_b(\hat{R})$, then $\chi_a(\hat{R})\chi_b(\hat{R})$ will equal -1 for some symmetry operation $\hat{R}$, and the only way that S_{ij} can equal $-S_{ij}$ in Equation 12.28 is for S_{ij} to equal zero. Thus, we have proved (at least for one-dimensional irreducible representations) one of the most useful results of group theory; namely, that S_{ij} must necessarily be equal to zero if ϕ_i^* and ϕ_j are bases of different irreducible representations.

Let's apply this result to the H_2O molecule (which lies in the y-z plane, Figure 12.6a) and evaluate S_{ij} for a $2p_x$ orbital on the oxygen atom ($2p_{x\text{O}}$) and the sum of the $1s$ orbitals on the hydrogen atoms ($1s_{\text{H}_\text{A}} + 1s_{\text{H}_\text{B}}$). This linear combination of hydrogen $1s$ orbitals is symmetric under all four operations of the $\mathbf{C}_{2v}$ point group, and so transforms as A_1. We chose $1s_{\text{H}_\text{A}} + 1s_{\text{H}_\text{B}}$ rather than $1s_{\text{H}_\text{A}}$ or $1s_{\text{H}_\text{B}}$ individually for this very reason. The $2p_x$ orbital on the oxygen atom transforms as x, which transforms as B_1 according to Table 12.7. Therefore, we can say that the overlap integral of $2p_{x\text{O}}$ and $1s_{\text{H}_\text{A}} + 1s_{\text{H}_\text{B}}$ is zero by symmetry. Table 12.7 shows that the same is true for $2p_{y\text{O}}$, but not for $2p_{z\text{O}}$.

EXAMPLE 12–14

Show that the overlap integral involving $2p_{x\text{N}}$ and $1s_{\text{H}_\text{A}} + 1s_{\text{H}_\text{B}} + 1s_{\text{H}_\text{C}}$ in the NH_3 molecule ($\mathbf{C}_{3v}$) is equal to zero.

SOLUTION: The linear combination $1s_{\text{H}_\text{A}} + 1s_{\text{H}_\text{B}} + 1s_{\text{H}_\text{C}}$ belongs to the totally symmetric irreducible representation A_1 and, according to Table 12.9, $2p_{x\text{N}}$ belongs to E. Therefore, the overlap integral is equal to zero.

The other integrals in a secular determinant are the H_{ij} in Equation 12.24. The molecular Hamiltonian operator is symmetric under all the group operations of the