6

SYMMETRY-ADAPTED LINEAR COMBINATIONS

6.1 INTRODUCTORY REMARKS

In nearly all of the ways in which chemists employ symmetry restrictions to aid them in understanding chemical bonding and molecular dynamics—for example, constructing hybrid orbitals, constructing molecular orbitals (MOs), finding proper orbital sets under the action of a ligand field, and analyzing the vibrations of molecules, to name those subjects which will be covered explicitly in later chapters of this book—there is a common problem. This problem is to take one or more sets of orthonormal functions, which are generally either atomic orbitals (AOs) or internal coordinates of a molecule, and to make orthonormal linear combinations of them in such a way that the combinations form bases for irreducible representations of the symmetry group of the molecule.

It will be obvious from the content of Chapter 5 why such combinations are desired. First, only such functions can, in themselves, constitute acceptable solutions to the wave equation or be directly combined to form acceptable solutions, as shown in Section 5.1. Second, only when the symmetry properties of wave functions are defined explicitly, in the sense of their being bases for irreducible representations, can we employ the theorems of Section 5.2 in order to determine without numerical computations which integrals or matrix elements in the problem are identically zero.

The kind of functions we need may be called *symmetry-adapted linear combinations* (SALCs). It is the purpose of this chapter to explain and illustrate the methods for constructing them in a general way. The details of adaptation to particular classes of problems will then be easy to explain as the needs arise.

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The fundamental, universally applicable tool for constructing SALCs is the *projection operator*. A complete projection operator is capable of generating a complete set of SALCs without, so to speak, human intervention. You just put the machine in gear, push the start button, and collect the answer. However, complete projection operators require a knowledge of the entire matrix for each operation. In practice, we prefer to employ the usual character tables which provide only the characters of the matrices. There is an "incomplete" projection operator that functions by using only the characters, but since there is no such thing as a free lunch, (not even with the help of group theory) one cannot automatically obtain complete SALCs with these operators. To obtain the complete result in cases of two- and higher-dimensional representations, "human intervention" is required. In the next section, we shall show how both the complete and the incomplete projection operators are derived. We shall then show how they work, in progressively more elaborate cases, with particular emphasis on showing how the incomplete operators in conjunction with standard character tables can always provide a complete set of SALCs.

6.2 DERIVATION OF PROJECTION OPERATORS

Let us assume that we have an orthonormal set of l_i functions $\phi_1^i, \phi_2^i, \ldots, \phi_{l_i}^i$, which form a basis for the ith irreducible representation (of dimension l_i) of a group of order h. For any operator, $\hat{R}$, in the group we may then, by definition, write

$$\hat{R}\phi_t^i = \sum_s \phi_s^i \Gamma(R)_{st}^i \tag{6.2-1}$$

This equation is then multiplied by $[\Gamma(R)_{s't'}^i]^*$, and each side summed over all operations in the group, giving

$$\sum_R [\Gamma(R)_{s't'}^i]^* \hat{R}\phi_t^i = \sum_R \sum_s \phi_s^i \Gamma(R)_{st}^i [\Gamma(R)_{s't'}^i]^* \tag{6.2-2}$$

We note that the ϕ_s^i's are functions independent of R; hence the right side of 6.2-2 may be rewritten as

$$\sum_s \phi_s^i \sum_R \Gamma(R)_{st}^i [\Gamma(R)_{s't'}^i]^*$$

Thus, we have a series of l_i terms, each of which is a ϕ_s^i multiplied by a coefficient; each coefficient is itself expressed as a sum of products over the operations $\hat{R}$ in the group. These coefficients, however, are governed by the

great orthogonality theorem (page 81), which states that

$$\sum_R \Gamma(R)^i_{st}[\Gamma(R)^{i'}_{s't'}]^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij}\delta_{ss'}\delta_{tt'}$$

Thus all ϕ^i_s except $\phi^{i'}_{s'}$ have coefficients of zero, and only when $i = j$ and $t = t'$ can even the term in $\phi_{s'}$ survive. Thus 6.2-2 simplifies to

$$\sum_R [\Gamma(R)^{i'}_{s't'}]^* \hat{R}\phi^i_t = \left(\frac{h}{l_j}\right) \phi^{i'}_{s'}\delta_{ij}\delta_{tt'} \tag{6.2-3}$$

We now introduce the symbol

$$\hat{P}^{i'}_{s't'} = \frac{l_j}{h} \sum_R [\Gamma(R)^{i'}_{s't'}]^* \hat{R} \tag{6.2-4}$$

and rewrite 6.2-3 as

$$\hat{P}^{i'}_{s't'}\phi^i_t = \phi^{i'}_{s'}\delta_{ij}\delta_{tt'} \tag{6.2-5}$$

The operator $\hat{P}^{i'}_{s't'}$ is called a projection operator. It may be applied to an arbitrary function ϕ^i_t, and only if that function itself or some term in it happens to be $\phi^{i'}_{t'}$. will the result be other than zero. If $\phi^{i'}_{t'}$ is a component of the arbitrary function, $\phi^{i'}_{s'}$ will be "projected" out of it and the rest will be abolished. Thus, we have

$$\hat{P}^{i'}_{s't'}\phi^{i'}_{t'} = \phi^{i'}_{s'}$$

In the very important special case where we use $\hat{P}^{i'}_{t't'}$ we have

$$\hat{P}^{i'}_{t't'}\phi^i_t = \phi^{i'}_{t'}\delta_{ij}\delta_{tt'} \tag{6.2-6}$$

which means that $\hat{P}^j_{l'l'}$ projects $\phi^j_{l'}$ out of an arbitrary function ϕ^j_l. Thus, by using the l_j projection operators based on the l_j diagonal matrix elements, we may generate from some arbitrary function, ϕ^j_l, the functions that form a basis for the jth irreducible representation.

An Illustrative Application of the Complete Projection Operator

To illustrate how 6.2-6 works, let us consider the general function, $xz + yz + z^2$, in the group C_{3v} (which is isomorphous to $G^{(1)}_6$). We shall use the projection operators to obtain from this arbitrary function a pair of functions which form a basis for the E representation. The matrices for this representation are given in Table 6.1. Table 6.2 shows how the arbitrary function $xz + yz + z^2$ is transformed by each of the six symmetry operators in the group.

Table 6.1 Matrices for the E Representation of the Group C_{3v}

Operation	Matrix	Operation	Matrix
E	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\sigma_v(xz)$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$
C_3	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	σ'_v	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$
C_3^2	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	σ''_v	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$

We shall first use the projection operator $\hat{P}^{E}_{11}$.

$$\begin{aligned}\hat{P}^{E}_{11}(xz + yz + z^2) = \tfrac{2}{6}\{&(1)(xz + yz + z^2)\\ &+ (-\tfrac{1}{2})[-\tfrac{1}{2}(1 + \sqrt{3})xz + \tfrac{1}{2}(\sqrt{3} - 1)yz + z^2]\\ &+ (-\tfrac{1}{2})[\tfrac{1}{2}(\sqrt{3} - 1)xz - \tfrac{1}{2}(1 + \sqrt{3})yz + z^2]\\ &+ (1)(xz - yz + z^2)\\ &+ (-\tfrac{1}{2})[-\tfrac{1}{2}(1 + \sqrt{3})xz + \tfrac{1}{2}(1 - \sqrt{3})yz + z^2]\\ &+ (-\tfrac{1}{2})[\tfrac{1}{2}(\sqrt{3} - 1)xz + \tfrac{1}{2}(1 + \sqrt{3})yz + x^2]\}\end{aligned}$$

We now collect terms. The coefficients of the xz, yz, and z^2 terms are as follows:

$$\begin{aligned}xz:\ &\tfrac{2}{6}[1 + \tfrac{1}{4}(1 + \sqrt{3}) - \tfrac{1}{4}(\sqrt{3} - 1) + 1 + \tfrac{1}{4}(1 + \sqrt{3}) - \tfrac{1}{4}(\sqrt{3} - 1)]\\ &= \tfrac{2}{6}[1 + \tfrac{1}{4} + \tfrac{1}{4} + 1 + \tfrac{1}{4} + \tfrac{1}{4} + \sqrt{3}(\tfrac{1}{4} - \tfrac{1}{4} + \tfrac{1}{4} - \tfrac{1}{4})]\\ &= \tfrac{2}{6}(3 + 0) = 1\end{aligned}$$

$$\begin{aligned}yz:\ &\tfrac{2}{6}[1 - \tfrac{1}{4}(\sqrt{3} - 1) + \tfrac{1}{4}(1 + \sqrt{3}) - 1 - \tfrac{1}{4}(1 - \sqrt{3}) - \tfrac{1}{4}(1 + \sqrt{3})]\\ &= \tfrac{2}{6}[1 + \tfrac{1}{4} + \tfrac{1}{4} - 1 - \tfrac{1}{4} - \tfrac{1}{4} + \sqrt{3}(-\tfrac{1}{4} + \tfrac{1}{4} + \tfrac{1}{4} - \tfrac{1}{4})]\\ &= \tfrac{2}{6}(0) = 0\end{aligned}$$

$$z^2:\ \tfrac{2}{6}(1 - \tfrac{1}{2} - \tfrac{1}{2} + 1 - \tfrac{1}{2} - \tfrac{1}{2}) = \tfrac{2}{6}(0) = 0$$

Table 6.2 Transformations of Some Simple Functions of x, y, and z

	Functions			
Operator	x	y	z	$xz + yz + z^2$
E	x	y	z	$xz + yz + z^2$
C_3	$\tfrac{1}{2}(-x + \sqrt{3}y)$	$\tfrac{1}{2}(-y - \sqrt{3}x)$	z	$\tfrac{1}{2}[-(1 + \sqrt{3})xz + (\sqrt{3} - 1)yz] + z^2$
C_3^2	$\tfrac{1}{2}(-x - \sqrt{3}y)$	$\tfrac{1}{2}(-y + \sqrt{3}x)$	z	$\tfrac{1}{2}[(\sqrt{3} - 1)xz - (1 + \sqrt{3})yz] + z^2$
$\sigma_v(xz)$	x	$-y$	z	$xz - yz + z^2$
σ_v'	$\tfrac{1}{2}(-x - \sqrt{3}y)$	$\tfrac{1}{2}(y - \sqrt{3}x)$	z	$\tfrac{1}{2}[-(1 + \sqrt{3})xz + (1 - \sqrt{3})yz] + z^2$
σ_v''	$\tfrac{1}{2}(-x + \sqrt{3}y)$	$\tfrac{1}{2}(y + \sqrt{3}x)$	z	$\tfrac{1}{2}[(\sqrt{3} - 1)xz + (1 + \sqrt{3})yz] + z^2$

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Next we use the projection operator, $\hat{P}^{E}_{22}$.

$$\begin{aligned}\hat{P}^{E}_{22}(xz + yz + z^2) = \tfrac{2}{6}\{&(1)(xz + yz + z^2)\\ &+ (-\tfrac{1}{2})[-\tfrac{1}{2}(1+\sqrt{3})xz + \tfrac{1}{2}(\sqrt{3}-1)yz + z^2]\\ &+ (-\tfrac{1}{2})[\tfrac{1}{2}(\sqrt{3}-1)xz - \tfrac{1}{2}(1+\sqrt{3})yz + z^2]\\ &+ (-1)(xz - yz + z^2)\\ &+ (\tfrac{1}{2})[-\tfrac{1}{2}(1+\sqrt{3})xz + \tfrac{1}{2}(1-\sqrt{3})yz + z^2]\\ &+ (\tfrac{1}{2})[\tfrac{1}{2}(\sqrt{3}-1)xz + \tfrac{1}{2}(1+\sqrt{3})yz + z^2]\}\end{aligned}$$

Again, we collect terms and evaluate the coefficients, obtaining

$$\begin{aligned}xz:\ &\tfrac{2}{6}[1 + \tfrac{1}{4}(1+\sqrt{3}) - \tfrac{1}{4}(\sqrt{3}-1) - 1 - \tfrac{1}{4}(1+\sqrt{3}) + \tfrac{1}{4}(\sqrt{3}-1)]\\ &= \tfrac{2}{6}[1 + \tfrac{1}{4} + \tfrac{1}{4} - 1 - \tfrac{1}{4} - \tfrac{1}{4} + \sqrt{3}(\tfrac{1}{4} - \tfrac{1}{4} - \tfrac{1}{4} + \tfrac{1}{4})]\\ &= \tfrac{2}{6}(0) = 0\end{aligned}$$

$$\begin{aligned}yz:\ &\tfrac{2}{6}[1 - \tfrac{1}{4}(\sqrt{3}-1) + \tfrac{1}{4}(1+\sqrt{3}) + 1 + \tfrac{1}{4}(1-\sqrt{3}) + \tfrac{1}{4}(1+\sqrt{3})]\\ &= \tfrac{2}{6}[1 + \tfrac{1}{4} + \tfrac{1}{4} + 1 + \tfrac{1}{4} + \tfrac{1}{4} + \sqrt{3}(-\tfrac{1}{4} + \tfrac{1}{4} - \tfrac{1}{4} + \tfrac{1}{4})]\\ &= \tfrac{2}{6}(3) = 1\end{aligned}$$

$$z^2:\ \tfrac{2}{6}(1 - \tfrac{1}{2} - \tfrac{1}{2} - 1 + \tfrac{1}{2} + \tfrac{1}{2}) = \tfrac{2}{6}(0) = 0$$

Thus we have projected out of the function $xz + yz + z^2$ the two functions xz and yz, which form a basis for the E representation. The component z^2 has been abolished; it cannot, in whole or in part, contribute to a basis set for the E representation.

The "Incomplete" Projection Operators

It will be clear from the foregoing discussion that in order to use the type of projection operator we have developed so far we need to know the individual diagonal elements of the matrices. This is inconvenient, since normally the only information readily accessible is the set of characters—the sum of all the diagonal matrix elements—for each matrix of the representation in question. For one-dimensional representations, this is a distinction without a difference, but for two- and three-dimensional cases it is advantageous to have a projection operator that employs only the characters. It is not difficult to derive the desired operator, beginning with the explicit expression for $\hat{P}^{i}_{l'l'}$, namely,

$$\hat{P}^{i}_{l'l'} = \frac{l_i}{h}\sum_{R}[\Gamma(R)^{i}_{l'l'}]^{*}\hat{R} \qquad (6.2\text{-}7)$$

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If we sum each side over all values of t', we obtain

$$\hat{P}^j = \sum_{t'} \hat{P}^j_{t't'} = \frac{l_j}{h} \sum_{t'} \sum_{R} [\Gamma(R)^j_{t't'}]^* \hat{R}$$

$$= \frac{l_j}{h} \sum_{R} \left\{ \sum_{t'} [\Gamma(R)^j_{t't'}]^* \right\} \hat{R}$$

$$\hat{P}^j = \frac{l_j}{h} \sum_{R} \chi(R)^j \hat{R} \qquad (6.2\text{-}8)$$

In this development we have employed the interchangeability of the order of the summations and the definition of the character of the matrix.

Let us now see what happens when we apply $\hat{P}^E$ to $xz + yz + z^2$.

$$\hat{P}^E(xz + yz + z^2) = \tfrac{2}{6}l(2)(xz + yz + z^2)$$

$$= \tfrac{1}{6}\{[\tfrac{1}{2}(1 + \sqrt{3})xz + \tfrac{1}{2}(\sqrt{3} - 1)yz + z^2] + [$$

$$+ \tfrac{1}{6}\{[\tfrac{1}{2}(\sqrt{3} - 1)xz - \tfrac{1}{2}(1 + \sqrt{3})yz + z^2] + [$$

$$+ 0 + 0\} + 0$$

$$+ \tfrac{1}{2}(1 + \sqrt{3}) - \tfrac{1}{2}(\sqrt{3} - 1)]xz = \tfrac{2}{6}\{[2$$

$$- \tfrac{1}{2}(\sqrt{3} - 1) + \tfrac{1}{2}(1 + \sqrt{3})]yz + [2$$

$$- 1 - 1)z^2\} + (2$$

$$+ 3yz + 0z^2) = \tfrac{2}{6}(3xz$$

$$yz = xz +$$

...eliminated the irrelevant part of the function. We see that this operation ha...
...mbination of the two separate functions, xz and yz, and projected out a linear co...
...obtain by employing the projection operators, $\hat{P}^E_{11}$ and $\hat{P}^E_{22}$. This should n...
...ıt be surprising. We obviously cannot get two separate results with only ...
...ne operator. Moreover, since the operator is

derived by adding the individual operators, a sum of the results given by the individual operators is what we must expect. Thus, the projection operators of the type $\hat{P}^j$ cannot be as powerful and explicit as those of the type $\hat{P}^j_{ii}$. However, they usually suffice for solving practical problems, as we shall demonstrate in the next section.

6.3 USING PROJECTION OPERATORS TO CONSTRUCT SALCs

The most important and frequent use for projection operators is to determine the proper way to combine atomic wave functions on individual atoms in a molecule into MOs that correspond to the molecular symmetry. As pointed out in Chapter 5, it is essential that valid MOs form bases for irreducible representations of the molecular point group. We encounter the problem of writing SALCs when we deal with molecules having sets of symmetry-equiv-

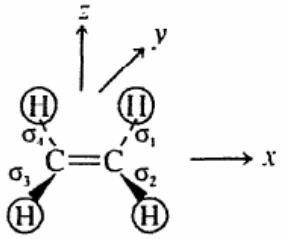
alent atoms (e.g., the C atoms of benzene, the F atoms of SF_6, or the Cl atoms of $Mo_2Cl_8^{4-}$) each contributing atomic wave functions to the formation of MOs. What we need to know are (1) the irreducible representations to which any given set of equivalent AOs will contribute, and (2) the explicit form of the linear combinations of atomic orbitals (LCAOs) that satisfy the symmetry properties of each representation. In short, we need SALCs constructed from atomic orbitals. In this section we shall present a number of examples of how this is done.

SALCs Belonging Only to One-Dimensional Representations: Sigma Bonding in C_2H_4

Clearly, for a one-dimensional representation the character and the full matrix are the same thing. Hence, the "incomplete" projection operator is "complete" in these cases, and will provide the appropriate SALC unambiguously and automatically. Let us illustrate by asking what SALCs can be formed by the 1*s* orbitals of the four hydrogen atoms in ethylene.

The three preliminary steps before the SALCs can actually be constructed are, in this and all other cases, the following:

1. We identify the point group: D_{2h}.
2. We use the four H 1*s* orbitals as the basis for a representation; we chose the coordinates and label the σ functions as shown below. It is necessary to



see how the set of four *basis functions*, that is, $\sigma_1 \cdots \sigma_4$, is affected by each symmetry operation. If we list the four basis functions as a column vector before and after the application of some symmetry operation, say $C_2(z)$, this is simply a way of stating that the $C_2(z)$ operation takes σ_1 from its initial position to the third position, σ_2 to the fourth position, σ_3 to the first position, and σ_4 to the second position.

$$\begin{bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\end{bmatrix} \longrightarrow \begin{bmatrix}\sigma_3\\ \sigma_4\\ \sigma_1\\ \sigma_2\end{bmatrix}$$

Before After

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We can now write a matrix that expresses this transformation:

$$\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \end{bmatrix} = \begin{bmatrix} \sigma_3 \\ \sigma_4 \\ \sigma_1 \\ \sigma_2 \end{bmatrix} \qquad \chi = 0$$

Clearly, the only way that any such matrix can have 1 rather than 0 at any diagonal position is when it carries one of the basis functions into itself. The original position to some $C_2(z)$ operation moves every basis function from its all positions. Its character where else, and thus has all of its 1's in off-diagon would thus have been recognized to be 0 without the entire matrix. The criterion is: *Any basis functi*

D_{2h} that leave *any* basis place, E and $\sigma(xy)$, and following reducible rep- *nothing to the character*. Thus the only operations ir function in place are the two that leave them all in these have a character of 4. Hence we obtain the resentation:

E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
4	0	0	0	0	4	0	0

3. We reduce this to its irreducible components: A_1, B_{1g}, B_{2u}, B_{3u}.

With these preliminaries settled, we now apply the appropriate projection operator, P^j (6.2-8) for each of these representations to one of the members of the *basis set*, that is, to any one of the four σ functions. In this and subsequent examples, we shall drop the numerical factor, l_j/h since we are interested only in the functional form of the SALC; its normalization is a trivial matter that can be attended to at the end. For each of the representations we have the following results:

$$\begin{aligned}\hat{P}^{A_{1g}}(\sigma_1) &= \overset{E}{(1)}\sigma_1 + \overset{C_2(z)}{(1)}\sigma_3 + \overset{C_2(y)}{(1)}\sigma_4 + \overset{C_2(x)}{(1)}\sigma_2 \\ &\quad \overset{i}{} + \overset{\sigma(xy)}{(1)}\sigma_3 + \overset{\sigma(xz)}{(1)}\sigma_1 + \overset{\sigma(yz)}{(1)}\sigma_2 + (1)\sigma_4 \\ &= 2(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \approx \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4\end{aligned}$$

$$\begin{aligned}\hat{P}^{B_{1g}}(\sigma_1) &= (1)\sigma_1 + (1)\sigma_3 + (-1)\sigma_4 + (-1)\sigma_2 \\ &\quad + (1)\sigma_3 + (1)\sigma_1 + (-1)\sigma_2 + (-1)\sigma_4 \\ &= 2(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) \approx \sigma_1 - \sigma_2 + \sigma_3 - \sigma_4\end{aligned}$$

$$\begin{aligned}\hat{P}^{B_{2u}}(\sigma_1) &= (1)\sigma_1 + (-1)\sigma_3 + (1)\sigma_4 + (-1)\sigma_2 \\ &\quad + (-1)\sigma_3 + (1)\sigma_1 + (-1)\sigma_2 + (1)\sigma_4 \\ &\approx \sigma_1 - \sigma_2 - \sigma_3 + \sigma_4\end{aligned}$$

$$\hat{P}^{B_{2u}}(\sigma_1) \approx \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4$$

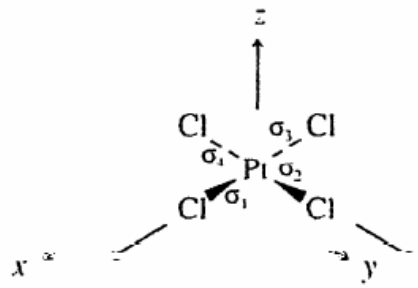
As a check on these results, each one can be subjected to the symmetry operations to be sure it responds (i.e., goes into $+1$ or -1 times itself) as required by the representation to which it belongs.

A Case of Involving a Two-Dimensional Representation: Sigma Bonding in $PtCl_4^{2-}$

We again take the first three steps and obtain:

Point Group: D_{4h}

Irreducible representations: $A_{1g} + B_{1g} + E_u$



For the two one-dimensional representations, the procedure is routine, but note that we must explicitly apply every one of the 16 operations in the class:

$$\hat{P}^{A_{1g}}(\sigma_1) \approx \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4$$

$$\hat{P}^{B_{1g}}(\sigma_1) \approx \sigma_1 - \sigma_2 + \sigma_3 - \sigma_4$$

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Now let us go after the E_u SALC. Note that only the operations E, C_4^2, i, and σ_h have nonzero characters, so these are the only ones that need to be considered. We obtain

$$\begin{aligned}\hat{P}^{E_u}(\sigma_1) &= \overset{E}{(2)}\sigma_1 + \overset{C_4^2}{(-2)}\sigma_3 + \overset{i}{(-2)}\sigma_3 + \overset{\sigma_h}{(2)}\sigma_1 \\ &\approx \sigma_1 - \sigma_3\end{aligned}$$

For a two-dimensional representation, we require two orthogonal functions, which jointly form a basis for the representation. We have one, but we require its partner. To obtain it, we recall that any member of a set of functions forming the basis for a representation must be affected by the symmetry operations of the group in one of two ways:

1. *It will go into ±1 times itself.*
2. It will go into another member of the set or a combination of members of the set.

If we look at the effect of the operations E, C_2, $2C_2'$, i, σ_h, and $2\sigma_v$, we see that they give $\pm 1(\sigma_1 - \sigma_3)$. This is as it should be, but uninformative. However, the remaining operations have the second type of effect, and thus enable us to find the partner function:

$$\begin{aligned}\hat{C}_4(\sigma_1 - \sigma_3) &= (\sigma_2 - \sigma_4) \quad \text{or} \quad -(\sigma_2 - \sigma_4) \\ \hat{C}_2''(\sigma_1 - \sigma_3) &= (\sigma_2 - \sigma_4) \quad \text{or} \quad -(\sigma_2 - \sigma_4) \\ \hat{S}_4(\sigma_1 - \sigma_3) &= (\sigma_2 - \sigma_4) \quad \text{or} \quad -(\sigma_2 - \sigma_4) \\ \hat{\sigma}_d(\sigma_1 - \sigma_3) &= (\sigma_2 - \sigma_4) \quad \text{or} \quad -(\sigma_2 - \sigma_4)\end{aligned}$$

Since only two orthogonal functions are needed to provide a basis for the E_u representations, we have clearly, in this simple case, reached the end of our quest. The two functions, in normalized form, that we require are

$$\frac{1}{\sqrt{2}}(\sigma_1 - \sigma_3) \quad \text{and} \quad \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_4)$$

An Example of SALCs for a Three-Dimensional Representation

In a hypothetical MH_6 molecule with O_h symmetry, it can be shown that the set of six M—H σ bonds provide the basis for the irreducible representations $A_{1g} + E_g + T_{1u}$. (As an exercise, show that this is so.) What are the expressions for the three SALCs corresponding to the T_{1u} representation?

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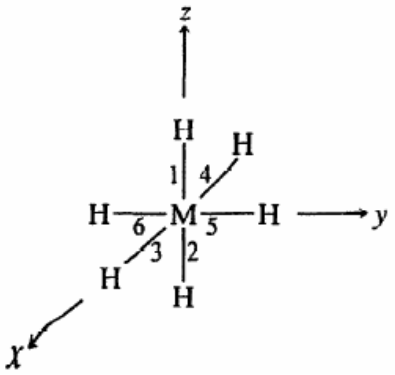
To solve this problem, we first recognize that we need not employ all of the 48 operations of O_h; instead, we can deal with the T_1 representation of the pure rotational subgroup O, which has only one half as many operations. Let us label axes and basis functions as shown in the sketch below:



If we apply the projection operator $\hat{P}^{T_1}$ to σ_1 and σ_2 we obtain:

$$\begin{aligned}\hat{P}^{T_1}(\sigma_1) &= 3\sigma_1 + (2\sigma_1 + 2\sigma_2 + 2\sigma_2) - (\sigma_1 + 2\sigma_2) \\ &\quad - (\sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 + 2\sigma_2) \\ &= 4\sigma_1 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6\end{aligned}$$

$$\hat{P}^{T_1}(\sigma_2) = 4\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6$$

By subtracting one of these from the other we obtain $4\sigma_1 - 4\sigma_2 \simeq \sigma_1 - \sigma_2$. Clearly, by proceeding in the same way with σ_3 and σ_4 and then with σ_5 and σ_6, we can obtain the following set of normalized SALCs:

$$\frac{1}{\sqrt{2}}(\sigma_1 - \sigma_2), \qquad \frac{1}{\sqrt{2}}(\sigma_3 - \sigma_4), \qquad \frac{1}{\sqrt{2}}(\sigma_5 - \sigma_6)$$

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These are clearly mutually orthogonal, and it is easy to show that they do, indeed, transform according to the T_{1u} representation of O_h. This last step is left as an exercise.

A Cyclic π System: π Orbitals for the Cyclopropenyl Group

The cyclopropenyl group, C_3H_3, is the simplest carbocycle with a delocalized π system and can serve as a prototype for this class of molecules. Let us see how the $p\pi$ orbitals of the individual carbon atoms can be combined into MOs—or at least the immediate precursors of actual π MOs. Cyclic π systems will be discussed in general in Chapter 7, and this illustration is intended only to demonstrate the use of projection operators in making SALCs of AOs on different atoms.

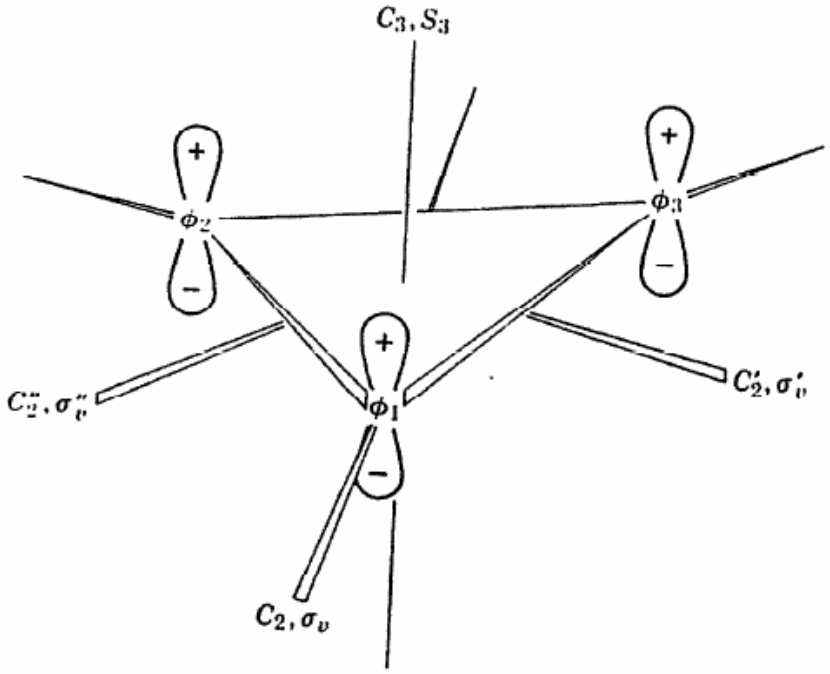
The usual preliminary steps before the SALCs can actually be set up give the following results.

Point group: D_{3h}

The representation (see sketch below)

E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
3	0	−1	−3	0	1

Irreducible components: $A_2'' + E''$



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Let us first apply the projection operator $\hat{P}^{A_2''}$ to ϕ_1. We thus obtain

$$\begin{aligned}\hat{P}^{A_2''}\phi_1 \approx\ & \phi_1 + \phi_2 + \phi_3 + \phi_1 + \phi_3 + \phi_2 + \phi_1 + \\ & \phi_2 + \phi_3 + \phi_1 + \phi_3 + \phi_2 \\ =\ & 4(\phi_1 + \phi_2 + \phi_3) \approx \phi_1 + \phi_2 + \phi_3\end{aligned}$$

The reader may demonstrate by applying the 12 group operations to it that this function does indeed form a basis for the A_2'' representation.

Clearly, if we multiply the A_2'' SALC by $1/\sqrt{3}$, it will be normalized. Thus the final result for A_2'' is $(1/\sqrt{3})(\phi_1 + \phi_2 + \phi_3)$.

For the E'' representation, using again ϕ_1, we have

$$\begin{aligned}\hat{P}^{E''}\phi_1 \approx\ & (2)\hat{E}\phi_1 + (-1)\hat{C}_3\phi_1 + (-1)\hat{C}_3^2\phi_1 + (0)\hat{C}_2\phi_1 \\ & + (0)\hat{C}_2'\phi_1 + (0)\hat{C}_2''\phi_1 + (-2)\hat{\sigma}_h\phi_1 + (1)\hat{S}_3\phi_1 \\ & + (1)\hat{S}_3^5\phi_1 + (0)\hat{\sigma}_v\phi_1 + (0)\hat{\sigma}_v'\phi_1 + (0)\hat{\sigma}_v''\phi_1 \\ =\ & 2\phi_1 - \phi_2 - \phi_3 + 2\phi_1 - \phi_2 - \phi_3 \approx 2\phi_1 - \phi_2 - \phi_3\end{aligned}$$

It is easy to show that the normalized function is $(1/\sqrt{6})(2\phi_1 - \phi_2 - \phi_3)$. As before, this is but *one* of *two* functions, which *together* form a basis for the E'' representation. We find its partner following the same method as before.

If we carry out a symmetry operation on one of the two functions, it will either go into ± 1 times itself, into its partner, or into a linear combination of itself and its partner. Let us chose an operation which does *not* convert it into $+1$ times itself, namely $\hat{C}_3$:

$$\hat{C}_3\left[\frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3)\right] \rightarrow \frac{1}{\sqrt{6}}(2\phi_2 - \phi_3 - \phi_1)$$

It may easily be shown that the second function is not ± 1 times the first, but in this case it is also not orthogonal to it, as the partner must be. The second function must therefore be a linear combination of the first and its partner, and we can find the expression for the partner by subtracting an appropriate multiple of the first one out of the second one, leaving the partner as the remainder.

This is most easily done by ignoring, for the moment, normalization, with the idea of attending to that at the end. Thus we proceed as follows:

$$\begin{aligned}&(2\phi_2 - \phi_3 - \phi_1) - (-\tfrac{1}{2})(2\phi_1 - \phi_2 - \phi_3) \\ &\quad = 2\phi_2 - \phi_3 - \phi_1 + \phi_1 - \tfrac{1}{2}\phi_2 - \tfrac{1}{2}\phi_3 \\ &\quad = \tfrac{3}{2}\phi_2 - \tfrac{3}{2}\phi_3 \approx \phi_2 - \phi_3\end{aligned}$$

This may be normalized to $(1/\sqrt{2})$ $(\phi_2 - \phi_3)$. It is orthogonal to the first function and is thus an acceptable partner:

$$\int \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3)\frac{1}{\sqrt{2}}(\phi_2 - \phi_3)\,d\tau$$
$$= \frac{1}{\sqrt{12}}\int (2\phi_1\phi_2 - 2\phi_1\phi_3 - \phi_2^2 + \phi_2\phi_3 - \phi_3\phi_2 + \phi_3^2)\,d\tau$$
$$= \frac{1}{\sqrt{12}}\left(2\int \phi_1\phi_2\,d\tau - 2\int \phi_1\phi_3\,d\tau - \int \phi_2^2\,d\tau + \ldots\right)$$
$$= \frac{1}{\sqrt{12}}[2(0) - 2(0) - 1 + 0 - 0 + 1] = 0$$

The reader may demonstrate that the pair of functions

$$\frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3), \qquad \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$$

do in fact form a basis for the matrices of the E'' representation and, moreover, that each of these is orthogonal to the SALC of A_2'' symmetry.

A General Simplification

The procedure just used, although routine and reliable, is lengthy, particularly for the two-dimensional representation. The results could have been obtained [illegible] by recognizing that the rotational symmetry, the behavior of [illegible] with respect [illegible]s upon rotation about a principal axis of order 3 or more alone [illegible] the SALC [illegible] basic form. Their behavior under the other symmetry operations fixes their [illegible]t consequence of the inherent symmetry of an individual orbital is a direc[illegible] [illegible]ese operations, σ_h or a C_2 passing through it, being added to the toward th[illegible] [illegible] properties under the pure rotations about the principal axis. Let symmetry[illegible]

us consider specifically the $C_3H_3^+$ case, where this can be seen by inspecting the D_{3h} character table. For all A-type representations, A_1', A_2', A_1'', and A_2'', the characters are the same for the C_3 and C_3^2 operations; similarly, the E' and E'' representations are identical within the subgroup C_3. The thing which decides that we are dealing specifically with A_2'' and E'' SALCs is the inherent nature of the $p\pi$ basis functions.

On the strength of the above considerations, a procedure that restricts attention to the pure rotational symmetry about the principal axis may be used to construct the SALCs. For C_3H_3, we use the group C_3. This group, like all uniaxial pure rotation groups, is Abelian. Its three operations fall into three classes, and it must have three irreducible representations of dimension 1. In general, a group C_n has n one-dimensional representations (cf. Section 4.5), so that what we show here for C_3 will be generalizable to all C_n groups.

In the subgroup C_3, the set of $p\pi$ orbitals of C_3H_3 spans the A and E representations. The latter, however, appears in the character table as two associated one-dimensional representations; a projection operator may be written for each of these one-dimensional components individually. Thus, we shall be able to obtain each of the SALCs belonging to the E representation directly and routinely, using projection operators. This is the advantage of using only the principal axis rotational symmetry. Let us now work through the algebra and see how much this trick expedites our task of constructing the SALCs.

Application of the projection operators P^A, $P^{E(1)}$, and $P^{E(2)}$ to ϕ_1 (neglecting constant numerical factors) gives:

$$\begin{aligned}
\hat{P}^A\phi_1 &\approx (1)\hat{E}\phi_1 + (1)\hat{C}_3\phi_1 + (1)\hat{C}_3^2\phi_1 \\
&= (1)\phi_1 + (1)\phi_2 + (1)\phi_3 \\
&= \phi_1 + \phi_2 + \phi_3 \\
\hat{P}^{E(1)}\phi_1 &\approx (1)\hat{E}\phi_1 + (\varepsilon)\hat{C}_3\phi_1 + (\varepsilon^*)\hat{C}_3^2\phi_1 \\
&= \phi_1 + \varepsilon\phi_2 + \varepsilon^*\phi_3 \\
\hat{P}^{E(2)}\phi_1 &\approx (1)\hat{E}\phi_1 + (\varepsilon^*)\hat{C}_3\phi_1 + (\varepsilon)\hat{C}_3^2\phi_1 \\
&= \phi_1 + \varepsilon^*\phi_2 + \varepsilon\phi_3
\end{aligned}$$

The A SALC has exactly the same form as we previously obtained for the A_2'' SALC, using full D_{3h} symmetry. The two E SALCs are actually satisfactory in the sense of being proper basis functions and being orthogonal to each other. However, we prefer to have real rather than complex coefficients. This change can be accomplished very simply because of the fact that the two sets of coefficients are arranged as pairs of complex conjugates (cf. Section 4.5). Thus, if we add them term by term, the imaginary components of each pair are eliminated, leaving a SALC with real coefficients. Also, if one set is subtracted, term by term, from the other, a set of pure imaginary coefficients will be obtained and the common factor i may be removed to leave another

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set of real coefficients. These addition and subtraction procedures are simply a case of forming new linear combinations of an initial set, and this is an entirely proper and rigorous thing to do. Thus, we add the two E SALCs obtained above:

$$\begin{array}{r} (\phi_1 + \varepsilon\phi_2 + \varepsilon^*\phi_3) \\ + (\phi_1 + \varepsilon^*\phi_2 + \varepsilon\phi_3) \\ \hline 2\phi_1 + (\varepsilon + \varepsilon^*)\phi_2 + (\varepsilon + \varepsilon^*)\phi_3 \end{array}$$

$$\begin{aligned} \varepsilon + \varepsilon^* &= (\cos 2\pi/3 + i \sin 2\pi/3) + (\cos 2\pi/3 - i \sin 2\pi/3) \\ &= 2 \cos 2\pi/3 = 2(-\tfrac{1}{2}) = -1 \end{aligned}$$

The first new SALC is therefore

$$2\phi_1 - \phi_2 - \phi_3$$

Next, we subtract the original E SALCs and divide out i:

$$\begin{array}{r} (\phi_1 + \varepsilon\phi_2 + \varepsilon^*\phi_3) \\ - (\phi_1 + \varepsilon^*\phi_2 + \varepsilon\phi_3) \\ \hline (\varepsilon - \varepsilon^*)\phi_2 - (\varepsilon - \varepsilon^*)\phi_3 \end{array}$$

$$\begin{aligned} \frac{(\varepsilon - \varepsilon^*)}{i} &= \frac{(\cos 2\pi/3 + i \sin 2\pi/3) - (\cos 2\pi/3 - i \sin 2\pi/3)}{i} \\ &= (2i \sin 2\pi/3)/i \\ &= 2 \sin 2\pi/3 = 2\left(\frac{\sqrt{3}}{2}\right) = \sqrt{3} \end{aligned}$$

The second new SALC, which should be orthogonal to the first and therefore its proper partner in forming a basis for the E representation, thus has the form

$$\phi_2 - \phi_3$$

Clearly, when the SALCs we have just obtained are properly normalized, they are identical to those previously obtained by using full D_{3h} symmetry. This second procedure, which was much simpler, may be summarized as follows:

1. An initial set of SALCs may be written down by inspection of the character table. Each one is of the form $a\phi_1 + b\phi_2 + c\phi_3$, with coefficients that are the characters for E, C_3, C_3^2.
2. The pairs of SALCs for the E representation are added and subtracted (dividing the result by i) to get two new orthogonal SALCs which have all real coefficients.
3. The SALCs are normalized.

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