

1.16: Symmetry Adapted Linear Combinations (SALCs)

Once we know the irreducible representations spanned by an arbitrary basis set, we can work out the appropriate linear combinations of basis functions that transform the matrix representatives of our original representation into block diagonal form (i.e. the *symmetry adapted linear combinations*). Each of the SALCs transforms as one of the irreducible representations of the reduced representation. We have already seen this in our NH_3 example. The two linear combinations of A_1 symmetry were s_N and $s_1 + s_2 + s_3$, both of which are symmetric under all the symmetry operations of the point group. We also chose another pair of functions, $2s_1 - s_2 - s_3$ and $s_2 - s_3$, which together transform as the symmetry species E .

To find the appropriate SALCs to reduce a matrix representation, we use *projection operators*. You will be familiar with the idea of operators from quantum mechanics. The operators we will be using here are not quantum mechanical operators, but the basic principle is the same. The projection operator to generate a SALC that transforms as an irreducible representation k is $\Sigma_g \chi_k(g)g$. Each term in the sum means ‘apply the symmetry operation g and then multiply by the character of g in irreducible representation k ’. Applying this operator to each of our original basis functions in turn will generate a complete set of SALCs, i.e. to transform a basis function f_i into a SALC f'_i , we use

$$f'_i = \sum_g \chi_k(g) g f_i \quad (16.1)$$

The way in which this operation is carried out will become much more clear if we work through an example. We can break down the above equation into a fairly straightforward ‘recipe’ for generating SALCs:

1. Make a table with columns labeled by the basis functions and rows labeled by the symmetry operations of the molecular point group. In the columns, show the effect of the symmetry operations on the basis functions (this is the $g f_i$ part of Equation 16.1).
2. For each irreducible representation in turn, multiply each member of the table by the character of the appropriate symmetry operation (we now have $\chi_k(g) g f_i$ for each operation). Summing over the columns (symmetry operations) generates all the SALCs that transform as the chosen irreducible representation.
3. Normalize the SALCs.

Earlier (see Section 10), we worked out the effect of all the symmetry operations in the C_{3v} point group on the (s_N, s_1, s_2, s_3) basis.

$$\begin{array}{ll} E & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3) \\ C_3^+ & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_3, s_1) \\ C_3^- & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_1, s_2) \\ \sigma_v & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_3, s_2) \\ \sigma'_v & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_1, s_3) \\ \sigma''_v & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_2, s_1) \end{array} \quad (16.2)$$

This is all we need to construct the table described in 1. above.

| | s_N | s_1 | s_2 | s_3 |
|--------------|-------|-------|-------|-------|
| E | s_N | s_1 | s_2 | s_3 |
| C_3^+ | s_N | s_2 | s_3 | s_1 |
| C_3^- | s_N | s_3 | s_1 | s_2 |
| σ_v | s_N | s_1 | s_3 | s_2 |
| σ'_v | s_N | s_2 | s_1 | s_3 |
| σ''_v | s_N | s_3 | s_2 | s_1 |

(16.3)

To determine the SALCs of A_1 symmetry, we multiply the table through by the characters of the A_1 irreducible representation (all of which take the value 1). Summing the columns gives

$$\begin{aligned}
 s_N + s_N + s_N + s_N + s_N + s_N &= 6s_N \\
 s_1 + s_2 + s_3 + s_1 + s_2 + s_3 &= 2(s_1 + s_2 + s_3) \\
 s_2 + s_3 + s_1 + s_3 + s_1 + s_2 &= 2(s_1 + s_2 + s_3) \\
 s_3 + s_1 + s_2 + s_2 + s_1 + s_3 &= 2(s_1 + s_2 + s_3)
 \end{aligned}
 \tag{16.4}$$

Apart from a constant factor (which doesn't affect the functional form and therefore doesn't affect the symmetry properties), these are the same as the combinations we determined earlier. Normalizing gives us two SALCs of A_1 symmetry.

$$\begin{aligned}
 \phi_1 &= s_N \\
 \phi_2 &= \frac{1}{\sqrt{3}}(s_1 + s_2 + s_3)
 \end{aligned}
 \tag{16.5}$$

We now move on to determine the SALCs of E symmetry. Multiplying the table above by the appropriate characters for the E irreducible representation gives

| | s_N | s_1 | s_2 | s_3 |
|--------------|--------|--------|--------|--------|
| E | $2s_N$ | $2s_1$ | $2s_2$ | $2s_3$ |
| C_3^+ | $-s_N$ | $-s_2$ | $-s_3$ | $-s_1$ |
| C_3^- | $-s_N$ | $-s_3$ | $-s_1$ | $-s_2$ |
| σ_v | 0 | 0 | 0 | 0 |
| σ'_v | 0 | 0 | 0 | 0 |
| σ''_v | 0 | 0 | 0 | 0 |

(16.6)

Summing the columns yields

$$\begin{aligned}
 2s_N - s_N - s_N &= 0 \\
 2s_1 - s_2 - s_3 & \\
 2s_2 - s_3 - s_1 & \\
 2s_3 - s_1 - s_2 &
 \end{aligned}
 \tag{16.7}$$

We therefore get three SALCs from this procedure. This is a problem, since the number of SALCs must match the dimensionality of the irreducible representation, in this case two. Put another way, we should end up with four SALCs in total to match our original number of basis functions. Added to our two SALCs of A_1 symmetry, three SALCs of E symmetry would give us five in total.

The resolution to our problem lies in the fact that the three SALCs above are not linearly independent. Any one of them can be written as a linear combination of the other two e.g. $(2s_1 - s_2 - s_3) = -(2s_2 - s_3 - s_1) - (2s_3 - s_1 - s_2)$. To solve the problem, we can either throw away one of the SALCs, or better, make two linear combinations of the three SALCs that are orthogonal to each other.⁵ e.g. if we take $2s_1 - s_2 - s_3$ as one of our SALCs and find an orthogonal combination of the other two (which turns out to be their difference), we have (after normalization)

$$\begin{aligned}
 \phi_3 &= \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3) \\
 \phi_4 &= \frac{1}{\sqrt{2}}(s_2 - s_3)
 \end{aligned}
 \tag{16.8}$$

These are the same linear combinations used in Section 12.

We now have all the machinery we need to apply group theory to a range of chemical problems. In our first application, we will learn how to use molecular symmetry and group theory to help us understand chemical bonding.

⁵ If we write the coefficients of s_1 , s_2 and s_3 for each SALC as a vector (a_1, a_2, a_3) , then when two SALCs are orthogonal, the dot product of their coefficient vectors $(a_1, a_2, a_3) \cdot (b_1, b_2, b_3) = (a_1b_1 + a_2b_2 + a_3b_3)$ is equal to zero.