1.11: Properties of Matrix Representations

Now that we've learnt how to create a matrix representation of a point group within a given basis, we will move on to look at some of the properties that make these representations so powerful in the treatment of molecular symmetry.

Similarity Transforms

Suppose we have a basis set $(x_1, x_2, x_3, \ldots x_n)$, and we have determined the matrix representatives for the basis in a given point group. There is nothing particularly special about the basis set we have chosen, and we could equally well have used any set of linear combinations of the original functions (provided the combinations were linearly independent). The matrix representatives for the two basis sets will certainly be different, but we would expect them to be related to each other in some way. As we shall show shortly, they are in fact related by a *similarity transform*. It will be far from obvious at this point why we would want to carry out such a transformation, but similarity transforms will become important later on when we use group theory to choose an optimal basis set with which to generate molecular orbitals.

Consider a basis set $\left(x_1', x_2', x_3', \ldots x_n' \right)$, in which each basis function x_i' is a linear combination of our original basis $(x_1, x_2, x_3, \ldots x_n)$.

$$x_j' = \Sigma_i x_i c_{ji} = x_1 c_{j1} + x_2 c_{j2} + \ldots \tag{11.1}$$

The c_{ji} appearing in the sum are coefficients; c_{ji} is the coefficient multiplying the original basis function x_i in the new linear combination basis function x_j'. We could also represent this transformation in terms of a matrix equation $\mathbf{x'} = \mathbf{x}C$:

$$(x_1', x_2', \ldots x_n') = (x_1, x_2, \ldots x_n) \begin{pmatrix} c_{11} & c_{12} & \ldots & c_{1n} \\ c_{21} & c_{22} & \ldots & c_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ c_{n1} & c_{n2} & \ldots & c_{nn} \end{pmatrix} \tag{11.2}$$

Now we look at what happens when we apply a symmetry operation g to our two basis sets. If $\Gamma(g)$ and $\Gamma'(g)$ are matrix representatives of the symmetry operation in the $\mathbf{x}$ and $\mathbf{x'}$ bases, then we have:

$$\begin{aligned} g\mathbf{x'} &= \mathbf{x'}\Gamma'(g) \\ g\mathbf{x}C &= \mathbf{x}C\Gamma'(g) && \text{since } \mathbf{x'} = \mathbf{x}C \\ g\mathbf{x} &= \mathbf{x}C\Gamma'(g)C^{-1} && \text{multiplying on the right by } C^{-1} \text{and using } CC^{-1} = I \\ &= \mathbf{x}\Gamma(g) \end{aligned} \tag{11.3}$$

We can therefore identify the similarity transform relating $\Gamma(g)$, the matrix representative in our original basis, to $\Gamma'(g)$, the representative in the transformed basis. The transform depends only on the matrix of coefficients used to transform the basis functions.

$$\Gamma(g) = C\Gamma'(g)C^{-1} \tag{11.4}$$

Also,

$$\Gamma'(g) = C^{-1}\Gamma(g)C \tag{11.5}$$

Characters of Representations

The trace of a matrix representative $\Gamma(g)$ is usually referred to as the *character* of the representation under the symmetry operation g. We will soon come to see that the characters of a matrix representation are often more useful than the matrix representatives themselves. Characters have several important properties.

1. The character of a symmetry operation is invariant under a similarity transform
2. Symmetry operations belonging to the same class have the same character in a given representation. Note that the character for a given class may be different in different representations, and that more than one class may have the same character.

Proofs of the above two statements are given in the Appendix.