1.12: Reduction of Representations I

Let us now go back and look at the C_{3v} representation we derived in 10.1 in more detail. If we look at the matrices carefully we see that they all take the same block diagonal form (a square matrix is said to be **block diagonal** if all the elements are zero except for a set of submatrices lying along the diagonal).

$$\begin{array}{cccccc}
\Gamma(E) & \Gamma(C_3^-) & \Gamma(C_3^+) & \Gamma(\sigma_v) & \Gamma(\sigma_v') & \Gamma(\sigma_v'') \\
\begin{pmatrix} 1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1 \end{pmatrix} &
\begin{pmatrix} 1&0&0&0\\0&0&1&0\\0&0&0&1\\0&1&0&0 \end{pmatrix} &
\begin{pmatrix} 1&0&0&0\\0&0&0&1\\0&1&0&0\\0&0&1&0 \end{pmatrix} &
\begin{pmatrix} 1&0&0&0\\0&1&0&0\\0&0&0&1\\0&0&1&0 \end{pmatrix} &
\begin{pmatrix} 1&0&0&0\\0&0&1&0\\0&1&0&0\\0&0&0&1 \end{pmatrix} &
\begin{pmatrix} 1&0&0&0\\0&0&0&1\\0&0&1&0\\0&1&0&0 \end{pmatrix} \\
\chi(E)=4 & \chi(C_3^+)=1 & \chi(C_3^-)=1 & \chi(\sigma_v)=2 & \chi(\sigma_v')=2 & \chi(\sigma_v'')=2
\end{array}$$

A block diagonal matrix can be written as the *direct sum* of the matrices that lie along the diagonal. In the case of the C_{3v} matrix representation, each of the matrix representatives may be written as the direct sum of a 1×1 matrix and a 3×3 matrix.

$$\Gamma^{(4)}(g)=\Gamma^{(1)}(g)\oplus\Gamma^{(3)}(g) \tag{1.12.1}$$

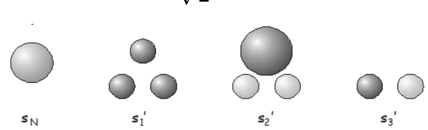
in which the bracketed superscripts denote the dimensionality of the matrices. Note that a direct sum is very different from ordinary matrix addition since it produces a matrix of higher dimensionality. A direct sum of two matrices of orders n and m is performed by placing the matrices to be summed along the diagonal of a matrix of order $n+m$ and filling in the remaining elements with zeroes.

The reason why this result is useful in group theory is that the two sets of matrices $\Gamma^{(1)}(g)$ and $\Gamma^{(3)}(g)$ also satisfy all of the requirements for a matrix representation. Each set contains the identity and an inverse for each member, and the members multiply together associatively according to the group multiplication table[3]. Recall that the basis for the original four-dimensional representation had the s orbitals (s_N, s_1, s_2, s_3) of ammonia as its basis. The first set of reduced matrices, $\Gamma^{(1)}(g)$, forms a one-dimensional representation with (s_N) as its basis. The second set, $\Gamma^{(3)}(g)$ forms a three-dimensional representation with the basis (s_1, s_2, s_3). Separation of the original representation into representations of lower dimensionality is called *reduction* of the representation. The two *reduced representations* are shown below.

$$\begin{array}{cccccccc}
g & E & C_3^+ & C_3^- & \sigma_v & \sigma_v' & \sigma_v'' & \\
\Gamma^{(1)}(g) & (1) & (1) & (1) & (1) & (1) & (1) & \text{1D representation spanned by } (s_N) \\
\Gamma^{(3)}(g) &
\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} &
\begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix} &
\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix} &
\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix} &
\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix} &
\begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix} &
\text{3D representation spanned by } (s_1, s_2, s_3)
\end{array}$$

The logical next step is to investigate whether or not the three dimensional representation $\Gamma^{(3)}(g)$ can be reduced any further. As it stands, the matrices making up this representation are not in block diagonal form (some of you may have noted that the matrices representing E and σ_v are block diagonal, but in order for a representation to be reducible *all* of the matrix representatives must be in the *same* block diagonal form) so the representation is not reducible. However, we can carry out a similarity transformation (see 10.1) to a new representation spanned by a new set of basis functions (made up of linear combinations of (s_1, s_2, s_3)), which *is* reducible. In this case, the appropriate (normalized) linear combinations to use as our new basis functions are

$$\begin{aligned} s_1' &= \frac{1}{\sqrt{3}}(s_1+s_2+s_3) \\ s_2' &= \frac{1}{\sqrt{6}}(2s_1-s_2-s_3) \\ s_3' &= \frac{1}{\sqrt{2}}(s_2-s_3) \end{aligned} \tag{1.12.2}$$



or in matrix form

$$\begin{array}{ccc} \left(s_1', s_2', s_3'\right) & = & \left(s_1, s_2, s_3\right) \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \\ \mathbf{x'} & = & \mathbf{x} \qquad C \end{array} \tag{1.12.3}$$

The matrices in the new representation are found from $\Gamma'(g) = C^{-1}\Gamma(g)C$ to be

$$\begin{array}{ccccccc} & E & C_3^+ & C_3^- & \sigma_v & \sigma_v' & \sigma_v'' \\ \Gamma^{(3)\prime}(g) & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} \end{array} \tag{1.12.4}$$

We see that each matrix is now in block diagonal form, and the representation may be reduced into the direct sum of a 1 x 1 representation spanned by $\left(s_1'\right)$ and a 2x2 representation spanned by $\left(s_2', s_3'\right)$. The complete set of reduced representations obtained from the original 4D representation is:

$$\begin{array}{ccccccc} E & C_3^+ & C_3^- & \sigma_v & \sigma_v' & \sigma_v'' & \\ (1) & (1) & (1) & (1) & (1) & (1) & \text{1D representation spanned by } \left(s_N\right) \\ (1) & (1) & (1) & (1) & (1) & (1) & \text{1D representation spanned by } \left(s_1'\right) \\ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} & \text{2D representation spanned by } \left(s_2', s_3'\right) \end{array} \tag{1.12.5}$$

This is as far as we can go in reducing this representation. None of the three representations above can be reduced any further, and they are therefore called *irreducible representations*, of the point group. Formally, a representation is an irreducible representation if there is no similarity transform that can simultaneously convert all of the representatives into block diagonal form. The linear combination of basis functions that converts a matrix representation into block diagonal form, allowing reduction of the representation, is called a *symmetry adapted linear combination (SALC)*.

[3] The 1x1 representation in which all of the elements are equal to 1 is sometimes called the *unfaithful representation*, since it satisfies the group properties in a fairly trivial way without telling us much about the symmetry properties of the group.