1.10: Matrix Representations of Groups

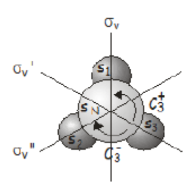
We are now ready to integrate what we have just learned about matrices with group theory. The symmetry operations in a group may be represented by a set of transformation matrices $\Gamma(g)$, one for each symmetry element g. Each individual matrix is called a **representative** of the corresponding symmetry operation, and the complete set of matrices is called a **matrix representation** of the group. The matrix representatives act on some chosen **basis set** of functions, and the actual matrices making up a given representation will depend on the basis that has been chosen. The representation is then said to **span** the chosen basis. In the examples above we were looking at the effect of some simple transformation matrices on an arbitrary vector (x, y). The basis was therefore a pair of unit vectors pointing in the x and y directions. In most of the examples we will be considering in this course, we will use sets of atomic orbitals as basis functions for matrix representations. Don't worry too much if these ideas seem a little abstract at the moment – they should become clearer in the next section when we look at some examples.

Before proceeding any further, we must check that a matrix representation of a group obeys all of the rules set out in the formal mathematical definition of a group.

1. The first rule is that the group must include the identity operation E (the 'do nothing' operation). We showed above that the matrix representative of the identity operation is simply the identity matrix. As a consequence, every matrix representation includes the appropriate identity matrix.
2. The second rule is that the combination of any pair of elements must also be an element of the group (the *group property*). If we multiply together any two matrix representatives, we should get a new matrix which is a representative of another symmetry operation of the group. In fact, matrix representatives multiply together to give new representatives in exactly the same way as symmetry operations combine according to the group multiplication table. For example, in the C_{3v} point group, we showed that the combined symmetry operation $C_3\sigma_v$ is equivalent to σ_v''. In a matrix representation of the group, if the matrix representatives of C_3 and σ_v are multiplied together, the result will be the representative of σ_v''.
3. The third rule states that every operation must have an inverse, which is also a member of the group. The combined effect of carrying out an operation and its inverse is the same as the identity operation. It is fairly easy to show that matrix representatives satisfy this criterion. For example, the inverse of a reflection is another reflection, identical to the first. In matrix terms we would therefore expect that a reflection matrix was its own inverse, and that two identical reflection matrices multiplied together would give the identity matrix. This turns out to be true, and can be verified using any of the reflection matrices in the examples above. The inverse of a rotation matrix is another rotation matrix corresponding to a rotation of the opposite sense to the first.
4. The final rule states that the rule of combination of symmetry elements in a group must be associative. This is automatically satisfied by the rules of matrix multiplication.

Example: a matrix representation of the C_{3v} point group (the ammonia molecule)

The first thing we need to do before we can construct a matrix representation is to choose a basis. For NH_3, we will select a basis (s_N, s_1, s_2, s_3) that consists of the valence s orbitals on the nitrogen and the three hydrogen atoms. We need to consider what happens to this basis when it is acted on by each of the symmetry operations in the C_{3v} point group, and determine the matrices that would be required to produce the same effect. The basis set and the symmetry operations in the C_{3v} point group are summarized in the figure below.



The effects of the symmetry operations on our chosen basis are as follows:

$$\begin{array}{ll} E & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_2, s_3) \\ C_3^+ & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_3, s_1) \\ C_3^- & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_1, s_2) \\ \sigma_v & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_1, s_3, s_2) \\ \sigma_v' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_2, s_1, s_3) \\ \sigma_v'' & (s_N, s_1, s_2, s_3) \rightarrow (s_N, s_3, s_2, s_1) \end{array} \tag{1.10.1}$$

By inspection, the matrices that carry out the same transformations are:

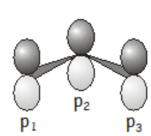
$$\begin{array}{lll} \Gamma(E) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & = (s_N, s_1, s_2, s_3) \\ \Gamma(C_3^+) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} & = (s_N, s_2, s_3, s_1) \\ \Gamma(C_3^-) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} & = (s_N, s_3, s_1, s_2) \\ \Gamma(\sigma_v) & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} & = (s_N, s_1, s_3, s_2) \\ \Gamma(\sigma_v') & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & = (s_N, s_2, s_1, s_3) \\ \Gamma(\sigma_v'') & (s_N, s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} & = (s_N, s_3, s_2, s_1) \end{array} \tag{1.10.2}$$

These six matrices therefore form a representation for the C_{3v} point group in the (s_N, s_1, s_2, s_3) basis. They multiply together according to the group multiplication table and satisfy all the requirements for a mathematical group.

> *We have written the vectors representing our basis as row vectors. This is important. If we had written them as column vectors, the corresponding transformation matrices would be the transposes of the matrices above, and would not reproduce the group multiplication table (try it as an exercise if you need to convince yourself).*

Example: a matrix representation of the C_{2v} point group (the allyl radical)

In this example, we'll take as our basis a p orbital on each carbon atom (p_1, p_2, p_3).



Note that the p orbitals are *perpendicular* to the plane of the carbon atoms (this may seem obvious, but if you're visualizing the basis incorrectly it will shortly cause you a not inconsiderable amount of confusion). The symmetry operations in the C_{2v} point group, and their effect on the three p orbitals, are as follows:

$$\begin{array}{ll} E & (p_1, p_2, p_3) \rightarrow (p_1, p_2, p_3) \\ C_2 & (p_1, p_2, p_3) \rightarrow (-p_3, -p_2, -p_1) \\ \sigma_v & (p_1, p_2, p_3) \rightarrow (-p_1, -p_2, -p_3) \\ \sigma_v' & (p_1, p_2, p_3) \rightarrow (p_3, p_2, p_1) \end{array} \tag{1.10.3}$$

The matrices that carry out the transformation are

$$\begin{array}{ll} \Gamma(E) & (p_1, p_2, p_3) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = (p_1, p_2, p_3) \\ \Gamma(C_2) & (p_1, p_2, p_3) \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix} = (-p_3, -p_2, -p_1) \\ \Gamma(\sigma_v) & (p_1, p_2, p_3) \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = (-p_1, -p_2, -p_3) \\ \Gamma(\sigma_v') & (p_1, p_2, p_3) \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} = (p_3, p_2, p_1) \end{array} \tag{1.10.4}$$