Matrices – A Primer

A matrix is commonly used to represent how equivalent coordinates or objects are <u>interchanged</u> by some operation.

The most common example is the rotation matrix to describe the effects of ~~rotating~~ moving a vector: $\begin{pmatrix} x \\ y \end{pmatrix}$ into a new vector $\begin{pmatrix} x' \\ y' \end{pmatrix}$

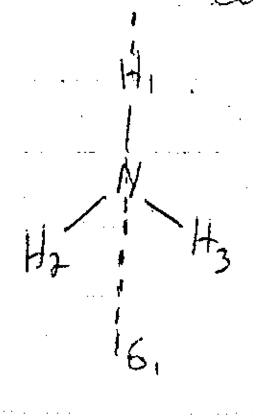
by <u>rotating</u> it an angle ϕ about $\begin{pmatrix} 0 \\ 0 \end{pmatrix}$

Here: $$\begin{pmatrix} \cos\phi & -\sin\phi \\ +\sin\phi & \cos\phi \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} x' \\ y' \end{pmatrix}$$

Hence a C_4 rotation: $\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$; a C_2: $\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$

Now anything else can be interchanged. If we represent the set of objects e.g. $\{X_1, X_2, \cdots, X_n\}$ as a column vector, their interchange can be represented as a matrix. For example:

let: $\begin{pmatrix} H_1 \\ H_2 \\ H_3 \end{pmatrix}$ be the vector of the set of three H-atoms in NH_3, then:



$$E: \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad C_3: \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}; \quad \sigma_1: \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

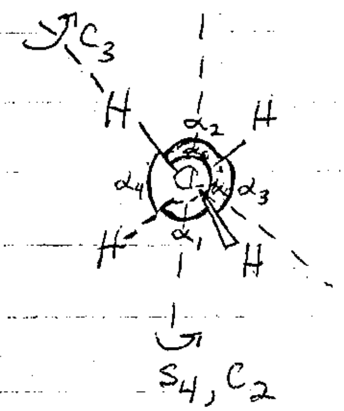
Since the three H-atoms have the symmetry of the NH_3 molecule, the matrices describing their interchange under C_{3v} symmetry operations will form a representation of the group. The characters of this reducible representation are: $\underline{\chi_{red}: 3 \; 0 \; 1}$

which can be decomposed: $\underline{\Gamma_{red} = A_1 + E}$ (try it!) by the usual formula

<u>Note</u>: a help in getting characters for these interchange matrices is to note that <u>only</u> <u>unmoved</u> atoms contribute to the diagonal

Using this reasoning, it is often possible to derive the characters of the interchange matrices without actually working them out.

To find the reducible representation of all the H-C-H angles of CH_4 – T_d:



There are six angles, none move under E: $\chi_E = 6$

under an S_4, all move: $\chi_{S_4} = 0$

under a C_2, 2 (α_1, α_2) remain the same: $\chi_{C_2} = 2$

under a C_3, all move: $\chi_{C_3} = 0$

under a σ, 2 remain: $\chi_\sigma = 2$

Td done probably: $\Gamma_r = A_1 + E + T_2$