Quantum Chemistry

Lecture 5
Group Theory

Matrix Representation
Cartesian Basis
Reducible and Irreducible Representations

NC State University

Matrix representation of a basis

The basis is comprised by the labels attached to objects. For molecules the objects can be:

1. Atoms
2. Coordinates
3. Orbitals
4. Bonds
5. Angles

The number of basis functions or labels is called the dimension.

For example, when considering molecular motions we Can assign coordinates x, y and z to each atom. There are three coordinates for N atoms to give a total dimension of 3N.

Matrix representation of the rotation operator

$$\begin{pmatrix} x_f \\ y_f \\ z_f \end{pmatrix} = \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$$

$$\begin{pmatrix} x_f \\ y_f \\ z_f \end{pmatrix} = C_3 \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$$

Matrix representation of the reflection operators

$$\begin{pmatrix} x_f \\ y_f \\ z_f \end{pmatrix} = \sigma_{V,yz} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$$

$$\begin{pmatrix} x_f \\ y_f \\ z_f \end{pmatrix} = \sigma_{V,xz} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$$

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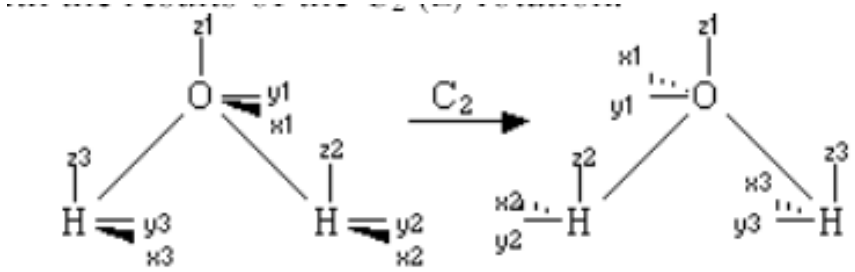
Matrix representation of the inversion operator

$$\begin{pmatrix} x_f \\ y_f \\ z_f \end{pmatrix} = i \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$$

Example: Motions of H_2O

The basis vectors are shown for the three atoms of water. Also shown is the result of the C_2 rotation:



If we examine the oxygen atom the rotation matrix can be formulated as:

$$\begin{bmatrix} x_j \\ y_j \\ z_j \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix}$$

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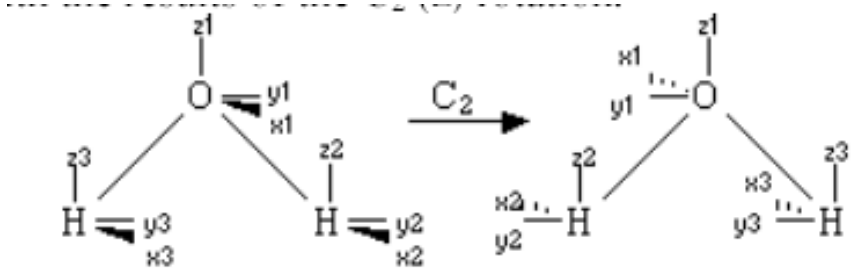

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The trace of this matrix is the sum of the diagonal elements.

Motions of H_2O

Since there are atoms the full matrix for H_2O is a 9x9:

$$C_2 \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & +1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & +1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & +1 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}$$

The hydrogen atoms are not on the diagonal since the atoms themselves are moved as a result of the C_2 rotation.

The trace of this matrix is –1. This is also called the character.

Motions of H_2O

We can consider also the result of the σv mirror plane, which is also a 9x9:

$$\sigma \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & +1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & +1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & +1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & +1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{pmatrix}$$

None of the atoms are moved by the symmetry operation so all of the submatrices representing the vectors lie along the diagonal. For this operation the trace (also known as the character) is +3.

Conclusions for symmetry operations

We can conclude with 2 general rules:

1. Only those atoms, which remain in the place following an operation can contribute to the trace.
2. Each atom contributes the same samount to the trace since all of the atoms have the same 3x3 matrix.

Using these principles we can see that σ_v' has a character of +1.
The identity always has a character equal to the number of basis functions. Here E = 9.

Using the character of the 4 symmetry operations of the C_{2v} point group we can construct a representation Γ.

Reducible and irreducible representations

We call the representation Γ a reducible representation. Here we write the reducible representation as:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ	9	-1	3	1

The irreducible representations form the basis of the point group in the same way that the vectors along x, y and z form the basis for three dimensional space.

H_2O belongs the point group C_{2v}. In this point group There are 4 irreducible representations, A_1, B_1, A_2, B_2. The decomposition of the reducible representation is a Unique determination of the irreducible reps (or irreps)z spanned by Γ.