Chapter 2 Representations of Groups

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Mathematical techniques of group theory makes it possible to describe and analyze some of the molecule’s chemically interesting properties.

The approach we take, in general, is to define a set of imagined vectors on the molecule’s various atoms to represent the properties of interest.

In order to apply symmetry arguments to the solution of molecular problems, we need an understanding of mathematical representations of groups - their construction, meaning, and manipulation.
2.1 Irreducible Representations

**Representation**: a set of symbols that will satisfy the multiplication table for the group.

The symbols themselves are called the **characters** of the representation.

The characters may be positive or negative integers, numeric values of certain trigonometric functions, imaginary number, or even square matrices.
2.1 Irreducible Representations

One such representation by making the trivial substitution of the integer 1 for each operation.

The set of all 1 characters makes the most fundamental representation for any group. This is called the totally symmetric representation. In the case of $C_{2v}$, this is designated by the symbol $A_1$. 

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v$</th>
<th>$\sigma'_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$E$</td>
<td>$C_2$</td>
<td>$\sigma_v$</td>
<td>$\sigma'_v$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>$C_2$</td>
<td>$E$</td>
<td>$\sigma'_v$</td>
<td>$\sigma_v$</td>
</tr>
<tr>
<td>$\sigma_v$</td>
<td>$\sigma_v$</td>
<td>$\sigma'_v$</td>
<td>$E$</td>
<td>$C_2$</td>
</tr>
<tr>
<td>$\sigma'_v$</td>
<td>$\sigma'_v$</td>
<td>$\sigma_v$</td>
<td>$C_2$</td>
<td>$E$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E = 1$</th>
<th>$C_2 = 1$</th>
<th>$\sigma_v = 1$</th>
<th>$\sigma'_v = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E = 1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$C_2 = 1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\sigma_v = 1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\sigma'_v = 1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
2.1 Irreducible Representations

This representation is given the symbol $A_2$. 

\[
\begin{array}{c|cccc}
C_{2v} & E & C_2 & \sigma_v & \sigma'_v \\
\hline
E & E & C_2 & \sigma_v & \sigma'_v \\
C_2 & C_2 & E & \sigma'_v & \sigma_v \\
\sigma_v & \sigma_v & \sigma'_v & E & C_2 \\
\sigma'_v & \sigma'_v & \sigma_v & C_2 & E \\
\end{array}
\]

\[
\begin{array}{c|cccc}
C_{2v} & E = 1 & C_2 = 1 & \sigma_v = -1 & \sigma'_v = -1 \\
\hline
E = 1 & 1 & 1 & -1 & -1 \\
C_2 = 1 & 1 & 1 & -1 & -1 \\
\sigma_v = -1 & -1 & -1 & 1 & 1 \\
\sigma'_v = -1 & -1 & -1 & 1 & 1 \\
\end{array}
\]

This representation is given the symbol $A_2$. 

\[
E = 1, \quad C_2 = -1, \quad \sigma_v = 1, \quad \sigma'_v = -1
\]

\[
E = 1, \quad C_2 = -1, \quad \sigma_v = -1, \quad \sigma'_v = 1
\]

$B_1$

$B_2$
2.1 Irreducible Representations

These four sets of \( \pm 1 \) characters are the only sets that meet the criterion.

Try this set

We know that \( EE = E \), but not in above.
2.1 Irreducible Representations

For $C_{2v}$ the representations we have found ($A_1, A_2, B_1, B_2$) are the simplest and most fundamental representations of $C_{2v}$.

For this reason they are called **irreducible representations** of the group.

We can list the characters and related properties of the irreducible representations of $C_{2v}$ in a tabular form, called a **character table**.

The labels for the irreducible representations ($A_1, A_2, B_1, B_2$) are the standard **Mulliken symbols**.

**Table 2.2** Partial Character Table for $C_{2v}$

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v$</th>
<th>$\sigma'_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>
In applying group theory to chemical problems we will need to use vector representations for molecular properties.

The four 1 X 1 operator matrices, which express the effects of the four operations of $C_{2v}$ on the unit vector $z$, are called transformation matrices.
2.2 Unit Vector Transformations

Each transformation matrix is identical to the character of the operation listed for the irreducible representation $A_1$ in the $C_{2v}$ character table.

In other words, the **characters of the $A_1$ representation** express the **transformation properties of a unit vector $z$ under the operations of $C_{2v}$**.

We say, then, that $z$ transforms as $A_1$ in $C_{2v}$ or $z$ belongs to the $A_1$ species of $C_{2v}$.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v$</th>
<th>$\sigma'_{v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>
2.2 Unit Vector Transformations

**Figure 2.1** Unit vectors z, x, and y (left to right).

<table>
<thead>
<tr>
<th>Operation</th>
<th>x becomes</th>
<th>In matrix notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>x</td>
<td>[+1]x</td>
</tr>
<tr>
<td>C₂</td>
<td>-x</td>
<td>[-1]x</td>
</tr>
<tr>
<td>σᵥ</td>
<td>x</td>
<td>[+1]x</td>
</tr>
<tr>
<td>σᵥ'</td>
<td>-x</td>
<td>[-1]x</td>
</tr>
</tbody>
</table>

**z axis**

**xz plane**

**yz plane**

x transforms as \(B_1\) in \(C_{2v}\)

<table>
<thead>
<tr>
<th>Operation</th>
<th>x becomes</th>
<th>In matrix notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>y</td>
<td>[+1]y</td>
</tr>
<tr>
<td>C₂</td>
<td>-y</td>
<td>[-1]y</td>
</tr>
<tr>
<td>σᵥ</td>
<td>-y</td>
<td>[-1]y</td>
</tr>
<tr>
<td>σᵥ'</td>
<td>y</td>
<td>[+1]y</td>
</tr>
</tbody>
</table>

**y transforms as \(B_2\) in \(C_{2v}\)**
In addition to linear unit vectors, we will need to consider vectors that suggest rotations about the three Cartesian axes.

Figure 2.2  A rotational vector, $R_z$.
2.3 Reducible Representations

Molecular properties are not always conveniently located along the axes of a Cartesian coordinate system.

We need to review some of the general properties of matrices and the rules for multiplying them.

\[
\begin{bmatrix}
a_{11} & a_{12} \\
a_{21} & a_{22} \\
a_{31} & a_{32}
\end{bmatrix}
\begin{bmatrix}
b_{11} & b_{12} & b_{13} \\
b_{21} & b_{22} & b_{23}
\end{bmatrix}
= 
\begin{bmatrix}
c_{11} & c_{12} & c_{13} \\
c_{21} & c_{22} & c_{23} \\
c_{31} & c_{32} & c_{33}
\end{bmatrix}
\begin{bmatrix}
(a_{11}b_{11} + a_{12}b_{21}) & (a_{11}b_{12} + a_{12}b_{22}) & (a_{11}b_{13} + a_{12}b_{23}) \\
(a_{21}b_{11} + a_{22}b_{21}) & (a_{21}b_{12} + a_{22}b_{22}) & (a_{21}b_{13} + a_{22}b_{23}) \\
(a_{31}b_{11} + a_{32}b_{21}) & (a_{31}b_{12} + a_{32}b_{22}) & (a_{31}b_{13} + a_{32}b_{23})
\end{bmatrix}
\]
2.3 Reducible Representations

The effect of the identity operation is expressed by following equation.

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
\end{bmatrix}
\begin{bmatrix}
x \\
y \\
z \\
\end{bmatrix}
= \begin{bmatrix}
(1)x + (0)y + (0)z \\
(0)x + (1)y + (0)z \\
(0)x + (0)y + (1)z \\
\end{bmatrix}
= \begin{bmatrix}
x \\
y \\
z \\
\end{bmatrix} \quad (2.4)
\]

Transformation matrix for the identity operation

\[
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1 \\
\end{bmatrix}
\begin{bmatrix}
x \\
y \\
z \\
\end{bmatrix}
= \begin{bmatrix}
(-1)x + (0)y + (0)z \\
(0)x + (-1)y + (0)z \\
(0)x + (0)y + (1)z \\
\end{bmatrix}
= \begin{bmatrix}
-x \\
-y \\
z \\
\end{bmatrix} \quad (2.5)
\]

Transformation matrix for the \( C_2 \) operation
### 2.3 Reducible Representations

The four $3 \times 3$ transformation matrices we obtain, which describe the effects of the operations of $C_{2v}$ on the coordinates of the general vector $\mathbf{v}$, constitute the characters of a representation of the group.
2.3 Reducible Representations

The set of four transformation matrices satisfies the criterion for a representation of $C_{2v}$.

Table 2.1 Multiplication Table for $C_{2v}$

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v$</th>
<th>$\sigma'_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$E$</td>
<td>$C_2$</td>
<td>$\sigma_v$</td>
<td>$\sigma'_v$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>$E$</td>
<td>$C_2$</td>
<td>$\sigma_v$</td>
<td>$\sigma'_v$</td>
</tr>
<tr>
<td>$\sigma_v$</td>
<td>$\sigma_v$</td>
<td>$\sigma_v$</td>
<td>$E$</td>
<td>$C_2$</td>
</tr>
<tr>
<td>$\sigma'_v$</td>
<td>$\sigma'_v$</td>
<td>$\sigma_v$</td>
<td>$C_2$</td>
<td>$E$</td>
</tr>
</tbody>
</table>

\[
\begin{array}{c}
E \\
C_2 \\
\sigma_v \\
\sigma'_v
\end{array}
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{bmatrix} =
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

(2.8)

\[
\begin{array}{c}
C_2 \\
\sigma_v \\
\sigma'_v
\end{array}
\begin{bmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{bmatrix} =
\begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

(2.9)
2.3 Reducible Representations

List the four transformation matrices as characters of a representation in a tabular form.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v$</th>
<th>$\sigma'_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_m$</td>
<td>$\begin{bmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{bmatrix}$</td>
<td>$\begin{bmatrix} -1 &amp; 0 &amp; 0 \ 0 &amp; -1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{bmatrix}$</td>
<td>$\begin{bmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 \ 0 &amp; 0 &amp; 1 \end{bmatrix}$</td>
<td>$\begin{bmatrix} -1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{bmatrix}$</td>
</tr>
</tbody>
</table>

We can recast it in a more convenient form by noting a common property of all the transformation matrices of which it is composed.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v$</th>
<th>$\sigma'_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_v$</td>
<td>3</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Trace or character of the matrix
2.3 Reducible Representations

$\Gamma_v$ is a reducible representation, which is *the sum of three of the irreducible representations of $C_{2v}$.*

Note that the three irreducible representations of which $\Gamma_v$ is composed are the three symmetry species by which the unit vectors $z$ ($A_1$), $x$ ($B_1$), and $y$ ($B_2$) transform.
2.4 More Complex Groups and Standard Character Tables

It consists of six operations \( h = 6 \) grouped into three classes.

From a geometrical point of view, operations in the same class can be converted into one another by changing the axis system.

A mathematically more general definition of class requires defining an equality called the similarity transform. The elements \( A \) and \( B \) belong to the same class if there is an element \( X \) within the group such that \( X^{-1}AX = B \), where \( X^{-1} \) is the inverse of \( X \) (i.e., \( XX^{-1} = X^{-1}X = E \)). If \( X^{-1}AX = B \), we say that \( B \) is the similarity transform of \( A \) by \( X \), or that \( A \) and \( B \) are conjugate to one another. We should note that the element \( X \) may in some cases be the same as either \( A \) or \( B \).
2.4 More Complex Groups and Standard Character Tables

Figure 2.4 Defining the orientations of the mirror planes of $C_{3v}$.

$C_{3v}$ is not Abelian

Two operations are members of the same class

<table>
<thead>
<tr>
<th>$C_{3v}$</th>
<th>$E$</th>
<th>$C_3$</th>
<th>$C_3^2$</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
<th>$\sigma_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$E$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
<td>$\sigma_1$</td>
<td>$\sigma_2$</td>
<td>$\sigma_3$</td>
</tr>
<tr>
<td>$C_3$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
<td>$E$</td>
<td>$\sigma_3$</td>
<td>$\sigma_1$</td>
<td>$\sigma_2$</td>
</tr>
<tr>
<td>$C_3^2$</td>
<td>$C_3^2$</td>
<td>$E$</td>
<td>$C_3$</td>
<td>$\sigma_2$</td>
<td>$\sigma_3$</td>
<td>$\sigma_1$</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>$\sigma_1$</td>
<td>$\sigma_2$</td>
<td>$\sigma_3$</td>
<td>$E$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
</tr>
<tr>
<td>$\sigma_2$</td>
<td>$\sigma_2$</td>
<td>$\sigma_3$</td>
<td>$\sigma_1$</td>
<td>$C_3^2$</td>
<td>$E$</td>
<td>$C_3$</td>
</tr>
<tr>
<td>$\sigma_3$</td>
<td>$\sigma_3$</td>
<td>$\sigma_1$</td>
<td>$\sigma_2$</td>
<td>$C_3$</td>
<td>$C_3^2$</td>
<td>$E$</td>
</tr>
</tbody>
</table>

$EC_3E = C_3$

$C_3^2C_3C_3 = C_3^2C_3^2 = C_3$

$C_3C_3C_3^2 = C_3E = C_3$

$\sigma_1C_3\sigma_1 = \sigma_1\sigma_3 = C_3^2$

$\sigma_2C_3\sigma_2 = \sigma_2\sigma_1 = C_3^2$

$\sigma_3C_3\sigma_3 = \sigma_3\sigma_2 = C_3^2$
It is a general relationship of group theory that the number of classes equals the number of irreducible representations of the group.

<table>
<thead>
<tr>
<th>Table 2.4</th>
<th>Character Table for the Point Group C$_{3v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{3v}$</td>
<td>E</td>
</tr>
<tr>
<td>A$_1$</td>
<td>1</td>
</tr>
<tr>
<td>A$_2$</td>
<td>1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
</tr>
</tbody>
</table>

There are three classes and three irreducible representations.

Mulliken symbol $E$ has a dimension of 2 ($d_i = 2$).
The irreducible representation $E$ is a doubly degenerate representation.
2.4 More Complex Groups and Standard Character Tables

The projection of \( \mathbf{v} \) on the z axis is unaffected by any of the symmetry operations of the group.

All operations affect x and y independently of z.

\[
\begin{bmatrix}
? & ? & 0 \\
? & ? & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
x \\
y \\
z
\end{bmatrix}
= 
\begin{bmatrix}
? \\
? \\
z
\end{bmatrix}
\]  

(2.11)
2.4 More Complex Groups and Standard Character Tables

Table 2.4 Character Table for the Point Group $C_{3v}$

<table>
<thead>
<tr>
<th>$C_{3v}$</th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

The transformation by $C_3$ is less straightforward. New coordinate requires an expression in both $x$ and $y$.

$E$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$ (2.12)

$\sigma_{xz}$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$ (2.13)

The transformation by $C_3$ is less straightforward. New coordinate requires an expression in both $x$ and $y$.

$$x' = \cos\frac{2\pi}{3}x - \sin\frac{2\pi}{3}y = -\frac{1}{2}x - \frac{\sqrt{3}}{2}y$$ (2.14)

$$y' = \sin\frac{2\pi}{3}x + \cos\frac{2\pi}{3}y = \frac{\sqrt{3}}{2}x - \frac{1}{2}y$$ (2.15)

Figure 2.5 Projection of $v$ in the $xy$ plane and the effect of $C_3$ in a counterclockwise direction.
2.4 More Complex Groups and Standard Character Tables

For a counterclockwise rotation about z through any angle $\theta$

$$\begin{bmatrix}
\frac{-1}{2} & -\frac{\sqrt{3}}{2} & 0 \\
\frac{\sqrt{3}}{2} & \frac{-1}{2} & 0 \\
0 & 0 & 1
\end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix}
\left(-\frac{x}{2} - \frac{\sqrt{3}y}{2}\right) \\
\left(\frac{\sqrt{3}x}{2} - \frac{y}{2}\right) \\
z
\end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \quad (2.16)$$

$$\begin{bmatrix}
\cos \theta & -\sin \theta & 0 \\
\sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \quad (2.17)$$
2.4 More Complex Groups and Standard Character Tables

Reduce this into its component irreducible representations by taking block diagonals of each matrix:

\[
\begin{array}{c|ccc}
C_{3\nu} & E & C_3 & \sigma_v \\
\hline
\Gamma_m & \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}
\end{array}
\]

Give the following two representations:

Doubly degenerate irreducible representation \( E \)
2.4 More Complex Groups and Standard Character Tables

The unit vectors \( x \) and \( y \) transform as a degenerate pair.
This means that in \( C_{3v} \) there is no difference in symmetry between the \( x \) and \( y \) directions, and they may be treated as equivalent.

In molecule with this symmetry, \( p_x \) and \( p_y \) orbitals on a central atom are required by symmetry to have the same energy and be indistinguishable.

<table>
<thead>
<tr>
<th>( C_{3v} )</th>
<th>( E )</th>
<th>( 2C_3 )</th>
<th>( 3\sigma_v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( E )</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

\( x \times y = (x^2 - y^2, xy)(xz, yz) \)

Totally symmetric representation
\( p_z \) orbital would be expected to have a different energy.

Transformation properties of the binary direct products of linear vectors.
Some of them correspond to the transformation properties of \( d \) orbitals.
2.4 More Complex Groups and Standard Character Tables

They arise because of the fundamental theorem of group theory that requires the number of representations in any group to be equal to the number of classes in the group.

Adding the complex-conjugate irreducible representations (two imaginary-characters) gives reducible representation (real number).

\[
e^p = \exp(2\pi p/n) = \cos 2\pi p/n + i \sin 2\pi p/n \tag{2.18}
\]
\[
e^{*p} = \exp(-2\pi p/n) = \cos 2\pi p/n - i \sin 2\pi p/n \tag{2.19}
\]

Combining Eqs. (2.18) and (2.19), we have

\[
e^p + e^{*p} = 2 \cos 2\pi p/n \tag{2.20}
\]
2.5 General Relationships of Irreducible Representations

The sum of the squares of the dimensions of all the irreducible representations is equal to the order of the group; that is,
\[ \sum \hat{d}_i^2 = h \]  
(2.21)

<table>
<thead>
<tr>
<th>(T_d)</th>
<th>(E)</th>
<th>8(C_3)</th>
<th>3(C_2)</th>
<th>6(S_4)</th>
<th>6(\sigma_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(A_2)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(E)</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(T_1)</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(T_2)</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ \sum \hat{d}_i^2 = \sum \left[ \chi_i(E) \right]^2 = 1^2 + 1^2 + 2^2 + 3^2 + 3^2 \]
\[ = 1 + 1 + 4 + 9 + 9 \]
\[ = 24 = h \]
2.5 General Relationships of Irreducible Representations

Great Orthogonality Theorem

2. The number of irreducible representations of a group is equal to the number of classes.

<table>
<thead>
<tr>
<th>$T_d$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6S_4$</th>
<th>$6\sigma_d$</th>
<th>$\Rightarrow h = 24$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$\Rightarrow d_i = 1$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$\Rightarrow d_i = 1$</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>$\Rightarrow d_i = 2$</td>
</tr>
<tr>
<td>$T_1$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$\Rightarrow d_i = 3$</td>
</tr>
<tr>
<td>$T_2$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$\Rightarrow d_i = 3$</td>
</tr>
</tbody>
</table>
2.5 General Relationships of Irreducible Representations

Great Orthogonality Theorem

3. In a given representation (irreducible or reducible) the characters for all operations belonging to the same class are the same.

<table>
<thead>
<tr>
<th>$T_d$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6S_4$</th>
<th>$6\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$T_1$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$T_2$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>
2.5 General Relationships of Irreducible Representations

Great Orthogonality Theorem

4. The sum of the squares of the characters in any irreducible representation equals the order of the group; that is,

\[ \sum_{R_c} g_c[\chi_{i}(R_c)]^2 = h \quad (2.24) \]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>8C3</th>
<th>3C2</th>
<th>6S4</th>
<th>6\sigma_d</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>T1</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

\[ \sum_{R_c} g_c[\chi_{T_2}(R_c)]^2 = (3)^2 + 8(0)^2 + 3(-1)^2 + 6(-1)^2 + 6(-1)^2 \]

\[ = 9 + 0 + 3 + 6 + 6 \]

\[ = 24 = h \]
2.5 General Relationships of Irreducible Representations

Great Orthogonality Theorem

5. Any two different irreducible representations are orthogonal, which means

\[ \sum_{R_c} g_c \chi_i(R_c) \chi_j(R_c) = 0 \]  \hspace{1cm} (2.25)

<table>
<thead>
<tr>
<th></th>
<th>(E)</th>
<th>(8C_3)</th>
<th>(3C_2)</th>
<th>(6S_4)</th>
<th>(6\sigma_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(A_2)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(E)</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(T_1)</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(T_2)</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

\[
\sum_{R_c} g_c \chi_i(R_c) \chi_j(R_c) = 1(1 \times 2) + 8(1 \times -1) + 3(1 \times 2) + 6(-1 \times 0) + 6(-1 \times 0) \\
= 2 - 8 + 6 + 0 + 0 \\
= 0
\]