Representations, Character Tables, and One Application of Symmetry

Chapter 4

Friday, October 2, 2015
Matrices and Matrix Multiplication

A matrix is an array of numbers, \( A_{ij} \)

\[
\begin{pmatrix}
-1 & 4 & 3 \\
-8 & -1 & 7 \\
2 & 14 & 1
\end{pmatrix}
\begin{pmatrix}
1 \\
2 \\
3
\end{pmatrix}
\]

To multiply two matrices, add the products, element by element, of each row of the first matrix with each column in the second matrix:

\[
\begin{pmatrix}
1 & 2 \\
3 & 4
\end{pmatrix} \times \begin{pmatrix}
1 & 2 \\
3 & 4
\end{pmatrix} = \begin{pmatrix}
(1\times1)+(2\times3) & (1\times2)+(2\times4) \\
(3\times1)+(4\times3) & (3\times2)+(4\times4)
\end{pmatrix} = \begin{pmatrix}
7 & 10 \\
15 & 22
\end{pmatrix}
\]

\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 2
\end{pmatrix} \times \begin{pmatrix}
1 \\
2 \\
3
\end{pmatrix} = \begin{pmatrix}
1 \\
-2 \\
6
\end{pmatrix}
\]
Transformation Matrices

Each symmetry operation can be represented by a 3×3 matrix that shows how the operation transforms a set of x, y, and z coordinates.

Let’s consider $C_{2h} \{E, C_2, i, \sigma_h\}$:

- **$C_2$**
  
<table>
<thead>
<tr>
<th>Transformation matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1 0 0</td>
</tr>
<tr>
<td>0 -1 0</td>
</tr>
<tr>
<td>0 0 1</td>
</tr>
</tbody>
</table>

  
  \[
  \begin{pmatrix}
  x' \\
  y' \\
  z'
  \end{pmatrix} = \begin{pmatrix}
  -1 & 0 & 0 \\
  0 & -1 & 0 \\
  0 & 0 & 1
  \end{pmatrix} \begin{pmatrix}
  x \\
  y \\
  z
  \end{pmatrix} = \begin{pmatrix}
  -x \\
  -y \\
  z
  \end{pmatrix}
  \]

- **$i$**
  
<table>
<thead>
<tr>
<th>Transformation matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1 0 0</td>
</tr>
<tr>
<td>0 -1 0</td>
</tr>
<tr>
<td>0 0 -1</td>
</tr>
</tbody>
</table>

  
  \[
  \begin{pmatrix}
  x' \\
  y' \\
  z'
  \end{pmatrix} = \begin{pmatrix}
  -1 & 0 & 0 \\
  0 & -1 & 0 \\
  0 & 0 & -1
  \end{pmatrix} \begin{pmatrix}
  x \\
  y \\
  z
  \end{pmatrix} = \begin{pmatrix}
  -x \\
  -y \\
  -z
  \end{pmatrix}
  \]
Representations of Groups

The set of four transformation matrices forms a matrix representation of the \( C_{2h} \) point group.

\[
\begin{align*}
E: & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & C_2: & \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & i: & \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \sigma_h: & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}
\end{align*}
\]

These matrices combine in the same way as the operations, e.g.,

\[
C_2 \times C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = E
\]

The sum of the numbers along each matrix diagonal (the character) gives a shorthand version of the matrix representation, called \( \Gamma \):

<table>
<thead>
<tr>
<th>( C_{2h} )</th>
<th>( E )</th>
<th>( C_2 )</th>
<th>( i )</th>
<th>( \sigma_h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma )</td>
<td>3</td>
<td>-1</td>
<td>-3</td>
<td>1</td>
</tr>
</tbody>
</table>

\( \Gamma \) (gamma) is a reducible representation b/c it can be further simplified.
The transformation matrices can be reduced to their simplest units (1×1 matrices in this case) by block diagonalization:

We can now make a table of the characters of each 1×1 matrix for each operation:

<table>
<thead>
<tr>
<th></th>
<th>$C_{2h}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$i$</th>
<th>$\sigma_h$</th>
<th>coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$x$</td>
</tr>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$y$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$z$</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>3</td>
<td>1</td>
<td>-1</td>
<td>-3</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

The three rows (labeled $B_u$, $B_u$, and $A_u$) are irreducible representations of the $C_{2h}$ point group. They cannot be simplified further. Their characters sum to give $\Gamma$. 
Irreducible Representations

The characters in the table show how each irreducible representation transforms with each operation.

<table>
<thead>
<tr>
<th>$C_{2h}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$i$</th>
<th>$\sigma_h$</th>
<th>coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$x$</td>
</tr>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$y$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$z$</td>
</tr>
</tbody>
</table>

1 = symmetric (unchanged); -1 = antisymmetric (inverted); 0 = neither

$A_u$ transforms like the $z$-axis: $E \rightarrow$ no change, $C_2 \rightarrow$ no change, $i \rightarrow$ inverted, $\sigma_h \rightarrow$ inverted

$A_u$ has the same symmetry as $z$ in $C_{2h}$
The characters in the table show how each irreducible representation transforms with each operation.

<table>
<thead>
<tr>
<th>irreducible representations</th>
<th>$C_{2h}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$i$</th>
<th>$\sigma_h$</th>
<th>coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td></td>
<td>$x$</td>
</tr>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td></td>
<td>$y$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>$z$</td>
</tr>
</tbody>
</table>

1 = symmetric (unchanged); -1 = antisymmetric (inverted); 0 = neither

$B_u$ transforms like $x$ and $y$: $E \rightarrow$ no change
$C_2 \rightarrow$ inverted
$i \rightarrow$ inverted
$\sigma_h \rightarrow$ no change

The two $B_u$ representations are exactly the same. We “merge” them to eliminate redundancy.
In the table, the characters show how each irreducible representation transforms with each operation. The symmetry operations are:

- $E$: symmetric (unchanged)
- $C_2$: inverted
- $i$: inverted
- $\sigma_h$: no change

### Table: Irreducible Representations

<table>
<thead>
<tr>
<th>Irreducible representations</th>
<th>Symmetry Operations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{2h}$</td>
</tr>
<tr>
<td>$B_u$</td>
<td></td>
</tr>
<tr>
<td>$A_u$</td>
<td></td>
</tr>
</tbody>
</table>

1 = symmetric (unchanged); -1 = antisymmetric (inverted); 0 = neither

The two $B_u$ representations are exactly the same. We “merge” them to eliminate redundancy.

$B_u$ transforms like $x$ and $y$:

- $E \rightarrow$ no change
- $C_2 \rightarrow$ inverted
- $i \rightarrow$ inverted
- $\sigma_h \rightarrow$ no change

The 1,5-dibromonaphthalene molecule is an example of a compound that uses $B_u$ irreducible representations.
Character Tables

List of the complete set of irreducible representations (rows) and symmetry classes (columns) of a point group.

<table>
<thead>
<tr>
<th>$C_{2h}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$i$</th>
<th>$\sigma_h$</th>
<th>linear</th>
<th>quadratic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$R_z$</td>
<td>$x^2, y^2, z^2, xy$</td>
</tr>
<tr>
<td>$B_g$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$R_x, R_y$</td>
<td>$xz, yz$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$z$</td>
<td></td>
</tr>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$x, y$</td>
<td></td>
</tr>
</tbody>
</table>

- The first column gives the Mulliken label for the representation
  - $A$ or $B = 1 \times 1$ representation that is symmetric (A) or anti-symmetric (B) to the principal axis.
  - $E = 2 \times 2$ representation (character under the identity will be 2)
  - $T = 3 \times 3$ representation (character under the identity will be 3)
  - For point groups with inversion, the representations are labelled with a subscript $g$ (gerade) or $u$ (ungerade) to denote symmetric or anti-symmetric with respect to inversion.
  - If present, number subscripts refer to the symmetry of the next operation class after the principle axis. For symmetric use subscript 1 and for anti-symmetric use subscript 2.
### Character Tables

List of the complete set of irreducible representations (rows) and symmetry classes (columns) of a point group.

<table>
<thead>
<tr>
<th>$C_{2h}$</th>
<th>$E$</th>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>$R_z$</td>
<td>$x^2, y^2, z^2, xy$</td>
</tr>
<tr>
<td>$B_g$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$R_x, R_y$</td>
<td>$xz, yz$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$z$</td>
<td>$x, y$</td>
</tr>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$x, y$</td>
<td></td>
</tr>
</tbody>
</table>

- The last two columns give functions (with an origin at the inversion center) that belong to the given representation (e.g., the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals are $A_g$, while the $p_z$ orbital is $A_u$).

![Diagram](image)
Properties of Character Tables

<table>
<thead>
<tr>
<th>$C_{2h}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$i$</th>
<th>$\sigma_h$</th>
<th>linear</th>
<th>quadratic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$R_z$</td>
<td>$x^2, y^2, z^2, xy$</td>
</tr>
<tr>
<td>$B_g$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$R_x, R_y$</td>
<td>$xz, yz$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td></td>
<td>$z$</td>
</tr>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td></td>
<td>$x, y$</td>
</tr>
</tbody>
</table>

- The total number of symmetry operations is the order ($h$). $h = 4$ in this case.
- Operations belong to the same class if they are identical within coordinate systems accessible by a symmetry operation. One class is listed per column.
- # irreducible representations = # classes (tables are square).
- One representation is totally symmetric (all characters = 1).
- $h$ is related to the characters ($\chi$) in the following two ways:
  
  \[ h = \sum_i [\chi_i(E)]^2 \]
  \[ h = \sum_R [\chi_i(R)]^2 \]

  where $i$ and $R$ are indices for the representations and the symmetry operations.
- Irreducible representations are orthogonal: $\sum_R \chi_i(R) \chi_j(R) = 0$ when $i \neq j$
Example

Let’s use the character table properties to finish deriving the $C_{2h}$ table. From the transformation matrices, we had:

<table>
<thead>
<tr>
<th>$C_{2h}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$i$</th>
<th>$\sigma_h$</th>
<th>coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>x, y</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>z</td>
</tr>
</tbody>
</table>

There must be four representations and one is totally symmetric, so:

<table>
<thead>
<tr>
<th>$C_{2h}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$i$</th>
<th>$\sigma_h$</th>
<th>coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>x, y</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>z</td>
</tr>
</tbody>
</table>

The fourth representation must be orthogonal to the other three and have $\chi(E) = 1$.

The only way to achieve this is if $\chi(C_2) = -1$, $\chi(i) = 1$, $\chi(\sigma_h) = -1$, giving a $B_g$
Let’s use the character table properties to finish deriving the $C_{2h}$ table.

From the transformation matrices, we had:

<table>
<thead>
<tr>
<th>$C_{2h}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$i$</th>
<th>$\sigma_h$</th>
<th>coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$x, y$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$z$</td>
</tr>
</tbody>
</table>

There must be four representations and one is totally symmetric, so:

<table>
<thead>
<tr>
<th>$C_{2h}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$i$</th>
<th>$\sigma_h$</th>
<th>coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>$B_g$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>$B_u$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$x, y$</td>
</tr>
<tr>
<td>$A_u$</td>
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<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$z$</td>
</tr>
</tbody>
</table>

The fourth representation must be orthogonal to the other three and have $\chi(E) = 1$.

The only way to achieve this is if $\chi(C_2) = -1, \chi(i) = 1, \chi(\sigma_h) = -1$, giving a $B_g$
# $C_{3v}$ Character Table

<table>
<thead>
<tr>
<th>$C_{3v}$</th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3\sigma_v$</th>
<th>linear</th>
<th>quadratic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$z$</td>
<td>$x^2 + y^2, z^2$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>$R_z$</td>
<td>(x, y), ($R_x$, $R_y$)</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>(x, y), ($R_x$, $R_y$), ($x^2 - y^2, xy), (xz, yz)$</td>
<td></td>
</tr>
</tbody>
</table>

The characters for $A_1$ and $E$ come from the transformation matrices:

**$E$:**

$$
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

**$C_3$:**

$$
\begin{pmatrix}
\cos\theta & -\sin\theta & 0 \\
\sin\theta & \cos\theta & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

\[
= \begin{pmatrix}
-1/2 & -\sqrt{3}/2 & 0 \\
\sqrt{3}/2 & -1/2 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

**$\sigma_v(xz)$:**

$$
\begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix}
$$

Rotation matrix about $z$-axis:

see website and p. 96

In block form:

**$E$:**

$$
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & [1]
\end{pmatrix}
$$

**$C_3$:**

$$
\begin{pmatrix}
\cos\theta & -\sin\theta & 0 \\
\sin\theta & \cos\theta & 0 \\
0 & 0 & [1]
\end{pmatrix}
$$

\[
= \begin{pmatrix}
-1/2 & -\sqrt{3}/2 & 0 \\
\sqrt{3}/2 & -1/2 & 0 \\
0 & 0 & [1]
\end{pmatrix}
\]

**$\sigma_v(xz)$:**

$$
\begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & [1]
\end{pmatrix}
$$

$x$ and $y$ are not independent in $C_{3v}$ – we get 2×2 (x, y) and 1×1 (z) matrices.
The third representation can be found from orthogonality and $\chi(E) = 1$.

### Note:

- $C_3$ and $C_3^2$ are identical after a $C_3$ rotation and are thus in the same class ($2C_3$)
- The three mirror planes are identical after $C_3$ rotations $\rightarrow$ same class ($3\sigma_v$)
- The $E$ representation is two dimensional ($\chi(E) = 2$), mixing $x, y$. This is a result of $C_3$.
- $x$ and $y$ considered together have the symmetry of the $E$ representation

Try proving that this character table actually has the properties expected of a character table.
Each molecule has a point group, the full set of symmetry operations that describes the molecule’s overall symmetry.

- You can use the decision tree to assign point groups.

Character tables show how the complete set of irreducible representations of a point group transforms under all of the symmetry classes of that group.

- The tables contain all of the symmetry information in convenient form.
- We will use the tables to understand bonding and spectroscopy.

To dig deeper, check out: Cotton, F. A. *Chemical Applications of Group Theory.*
Using Symmetry: Chirality

One use for symmetry is identifying chiral molecules

- To be chiral, a molecule must lack an improper rotation axis
- In other words, for a molecule to be chiral it must be in the $C_1$, $C_n$, or $D_n$ point groups (remember that $\sigma = S_1$ and $i = S_2$).
Using Symmetry: Chirality

One use for symmetry is identifying chiral molecules

- To be chiral, a molecule must lack an improper rotation axis
- In other words, for a molecule to be chiral it must be in the $C_1$, $C_n$, or $D_n$ point groups (remember that $\sigma = S_1$ and $i = S_2$).