Review of Matrices

A matrix is a rectangular array of numbers that combines with other such arrays according to specific rules.

\[
\begin{bmatrix}
  a_{11} & a_{12} & \cdots & a_{1n} \\
  a_{21} & a_{22} & \cdots & a_{2n} \\
  \vdots & \vdots & \ddots & \vdots \\
  a_{m1} & a_{m2} & \cdots & a_{mn}
\end{bmatrix}
\]

The dimension of a matrix is given as rows x columns; i.e., \( m \times n \).
Matrix Multiplication

If two matrices are to be multiplied together they must be *conformable*; i.e., the number of columns in the first (left) matrix must be the same as the number of rows in the second (right) matrix.

The product matrix has as many rows as the first matrix and as many columns as the second matrix.

\[
\begin{bmatrix}
  a_{11} & a_{12} \\
  a_{21} & a_{22} \\
  a_{31} & a_{32}
\end{bmatrix}
\begin{bmatrix}
  b_{11} & b_{12} & b_{13} \\
  b_{21} & b_{22} & b_{23} \\
  b_{31} & b_{32} & b_{33}
\end{bmatrix}
= 
\begin{bmatrix}
  c_{11} & c_{12} & c_{13} \\
  c_{21} & c_{22} & c_{23} \\
  c_{31} & c_{32} & c_{33}
\end{bmatrix}
\]

The elements of the product matrix, \(c_{ij}\), are the sums of the products \(a_{ik}b_{kj}\) for all values of \(k\) from 1 to \(m\); i.e.,

\[
c_{ij} = \sum_{k=1}^{m} a_{ik}b_{kj}
\]
Transformations of a General Vector in $C_{2v}$

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

\[
C_2 \quad \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}
\]

\[
\sigma_v = \sigma_{xz} \quad \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}
\]

\[
\sigma_v' = \sigma_{yz} \quad \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ y \\ z \end{bmatrix}
\]
A Representation with Matrices

<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>$\begin{bmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; -1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{bmatrix}$</td>
<td>$\begin{bmatrix} -1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{bmatrix}$</td>
</tr>
</tbody>
</table>

✓ These matrices combine with each other in the same ways as the operations, so they form a representation of the group.

✓ $\Gamma_m$ is a reducible representation

The character of a matrix (symbol chi, $\chi$) is the sum of the elements along the left-to-right diagonal (the trace) of the matrix.

$\chi(E) = 3 \quad \chi(C_2) = -1 \quad \chi(\sigma_v) = 1 \quad \chi(\sigma_v') = 1$

A more compact form of a reducible representation can be formed by using the characters of the full-matrix form of the representation.

✓ We will most often use this form of representation.

✓ The character form of a representation does not by itself conform to the multiplication table of the group; only the original matrix form does this.
A Representation from the Traces (Characters) of the Matrices

<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>

The characters of $\Gamma_v$ are the sums of the corresponding characters of the three irreducible representations $A_1 + B_1 + B_2$:

<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>$B_1$</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>
<tr>
<td>$\Gamma_v$</td>
<td>3</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

$\Gamma_v = A_1 + B_1 + B_2$

Breaking down $\Gamma_v$ into its component irreducible representations is called reduction.

The species into which $\Gamma_v$ reduces are the those by which the vectors $z$, $x$, and $y$ transform, respectively.
Reduction of $\Gamma_m$ by Block Diagonalization

<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></td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma_m$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Each diagonal element, $c_{ii}$, of each operator matrix expresses how one of the coordinates $x$, $y$, or $z$ is transformed by the operation.

- Each $c_{11}$ element expresses the transformation of the $x$ coordinate.
- Each $c_{22}$ element expresses the transformation of the $y$ coordinate.
- Each $c_{33}$ element expresses the transformation of the $z$ coordinate.

The set of four $c_{ii}$ elements with the same $i$ (across a row) is an irreducible representation.

The three irreducible representations found by block diagonalization of $\Gamma_m$ are the same as those found for $\Gamma_v$; i.e.,

$$\Gamma_m = A_1 + B_1 + B_2 = \Gamma_v$$

The reduction of a reducible representation in either full-matrix or character form gives the same set of component irreducible representations.
Dimensions of Representations

In a representation of matrices, such as $\Gamma_m$, the *dimension of the representation* is the order of the square matrices of which it is composed.

$$d\left(\Gamma_m\right) = 3$$

For a representation of characters, such as $\Gamma_v$, the dimension is the value of the character for the identity operation.

$$\chi(E) = 3 \quad \Rightarrow \quad d\left(\Gamma_v\right) = 3$$

The dimension of the reducible representation must equal the sum of the dimensions of all the irreducible representations of which it is composed.

$$d_r = \sum_i n_i d_i$$
More Complex Groups
and
Standard Character Tables

<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 group $C_{3v}$ has:
- Three classes of elements (symmetry operations).
- Three irreducible representations.
- One irreducible representation has a dimension of $d_i = 2$ (doubly degenerate).

The character table has a last column for direct product transformations.
Classes

Geometrical Definition (Symmetry Groups): Operations in the same class can be converted into one another by changing the axis system through application of some symmetry operation of the group.

Mathematical Definition (All Groups): 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.
- The element $X$ may in some cases be the same as either $A$ or $B$. 
Classes of $C_{3v}$ by Similarity Transforms

<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>

Take the similarity transforms on $C_3$ to find all members in its class:

- $EC_3E = C_3$
- $C_3^2C_3C_3 = C_3^2C_3^2 = C_3$
- $C_3C_3C_3^2 = C_3E = C_3$
- $\sigma_1C_3\sigma_1 = \sigma_1\sigma_3 = C_3^2$
- $\sigma_2C_3\sigma_2 = \sigma_2\sigma_1 = C_3^2$
- $\sigma_3C_3\sigma_3 = \sigma_3\sigma_2 = C_3^2$  ✓ Only $C_3$ and $C_3^2$

Take the similarity transforms on $\sigma_1$ to find all members in its class:

- $E\sigma_1E = \sigma_1$
- $C_3^2\sigma_1C_3 = C_3^2\sigma_2 = \sigma_3$
- $C_3\sigma_1C_3^2 = C_3\sigma_3 = \sigma_2$
- $\sigma_1\sigma_1\sigma_1 = \sigma_1E = \sigma_1$
- $\sigma_2\sigma_1\sigma_2 = \sigma_1C_3 = \sigma_2$
- $\sigma_3\sigma_1\sigma_3 = \sigma_1C_3^2 = \sigma_3$  ✓ Only $\sigma_1$, $\sigma_2$, and $\sigma_3$
Transformations of a General Vector in $C_{3v}$
The Need for a Doubly Degenerate Representation

No operation of $C_{3v}$ changes the $z$ coordinate.

チェック Every operation involves an equation of the form

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

チェック We only need to describe any changes in the projection of $v$ in the $xy$ plane.

チェック The operator matrix for each operation is generally unique, but all operations in the same class have the same character from their operator matrices.

チェック We only need to examine the effect of one operation in each class.
Transformations by $E$ and $\sigma_1 = \sigma_{xz}$

$E$

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

$\sigma_1 = \sigma_{xz}$

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1 \\
\end{bmatrix}
\begin{bmatrix}
x \\
y \\
z \\
\end{bmatrix} =
\begin{bmatrix}
x \\
-y \\
z \\
\end{bmatrix}
\]
Transformation by $C_3$

From trigonometry:

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

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

Therefore, the transformation matrix has nonzero off-diagonal elements:

$$\begin{bmatrix}
-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\
\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
x \\
y \\
z
\end{bmatrix}
= 
\begin{bmatrix}
\left( -\frac{x}{2} - \frac{\sqrt{3}y}{2} \right) \\
\left( \frac{\sqrt{3}x}{2} - \frac{y}{2} \right) \\
z
\end{bmatrix}
= 
\begin{bmatrix}
x' \\
y' \\
z'
\end{bmatrix}$$
**Reduction by Block Diagonalization**

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

The blocks must be the same size across all three matrices.

- The presence of nonzero, off-diagonal elements in the transformation matrix for $C_3$ restricts us to diagonalization into a 2x2 block and a 1x1 block.
- For all three matrices we must adopt a scheme of block diagonalization that yields one set of 2x2 matrices and another set of 1x1 matrices.
Representations of Characters

Converting to representations of characters gives a doubly degenerate irreducible representation and a nondegenerate representation.

\[
\begin{array}{c|ccc}
C_{3v} & E & 2C_3 & 3\sigma_v \\
\hline
\Gamma_{x,y} = E & 2 & -1 & 0 \\
\Gamma_z = A_1 & 1 & 1 & 1 \\
\end{array}
\]

Any property that transforms as \( E \) in \( C_{3v} \) will have a companion, with which it is degenerate, that will be symmetrically and energetically equivalent.

\[
\begin{array}{c|ccc|c|c}
C_{3v} & E & 2C_3 & 3\sigma_v & & \\
\hline
A_1 & 1 & 1 & 1 & z & x^2+y^2, z^2 \\
A_2 & 1 & 1 & -1 & R_z & \\
E & 2 & -1 & 0 & (x, y) (R_x, R_y) & (x^2-y^2, xy)(xz, yz) \\
\end{array}
\]

Unit vectors \( \mathbf{x} \) and \( \mathbf{y} \) are degenerate in \( C_{3v} \).

Rotational vectors \( R_x, R_y \) are degenerate in \( C_{3v} \).
Direct Product Listings

<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 last column of typical character tables gives the transformation properties of direct products of vectors.

✓ Among other things, these can be associated with the transformation properties of \( d \) orbitals in the point group.

Correspond to \( d \) orbitals: \( z^2, x^2-y^2, xy, xz, yz, 2z^2-x^2-y^2 \)

Do not correspond to \( d \) orbitals: \( x^2, y^2, x^2+y^2, x^2+y^2+z^2 \)
Complex-Conjugate Paired Irreducible Representations

Some groups have irreducible representations with imaginary characters in complex conjugate pairs:

\[ C_n (n \geq 3), \quad C_{nh} (n \geq 3), \quad S_{2n}, \quad T, \quad T_h \]

- The paired representations appear on successive lines in the character tables, joined by braces (\{ \} ).
- Each pair is given the single Mulliken symbol of a doubly degenerate representation (e.g., \( E, E_1, E_2, E', E'', E_g, E_u \)).
- Each of the paired complex-conjugate representations is an irreducible representation in its own right.
Combining Complex-Conjugate Paired Representations

It is sometimes convenient to add the two complex-conjugate representations to obtain a representation of real characters.

When the pair has \( \varepsilon \) and \( \varepsilon^* \) characters, where \( \varepsilon = \exp(2\pi i/n) \), the following identities are used in taking the sum:

\[
\varepsilon^p = \exp(2\pi p i/n) = \cos 2\pi p/n + i\sin 2\pi p/n
\]

\[
\varepsilon^{*p} = \exp(-2\pi p i/n) = \cos 2\pi p/n - i\sin 2\pi p/n
\]

which combine to give

\[
\varepsilon^p + \varepsilon^{*p} = 2\cos 2\pi p/n
\]

Example: In \( C_3 \), \( \varepsilon = \exp(2\pi i/3) \) and \( \varepsilon + \varepsilon^* = 2 \cos 2\pi/3 \).

\[
\begin{array}{ccc}
C_3 & E & C_3 & C_3^2 \\
E^a & 1 & \varepsilon & \varepsilon^* \\
E^b & 1 & \varepsilon^* & \varepsilon \\
\{E\} & 2 & 2 \cos 2\pi/3 & 2 \cos 2\pi/3 \\
\end{array}
\]

If complex-conjugate paired representations are combined in this way, realize that the real-number representation is a reducible representation.
Mulliken Symbols
Irreducible Representation Symbols

In non-linear groups:

- **A** nondegenerate; symmetric to $C_n$ ($\chi_{C_n} > 0$)
- **B** nondegenerate; antisymmetric to $C_n$ ($\chi_{C_n} < 0$)
- **E** doubly degenerate ($\chi_E = 2$)
- **T** triply degenerate ($\chi_E = 3$)
- **G** four-fold degenerate ($\chi_E = 4$) in groups $I$ and $I_h$
- **H** five-fold degenerate ($\chi_E = 5$) in groups $I$ and $I_h$

In linear groups $C_{\infty v}$ and $D_{\infty h}$:

- $\Sigma \equiv A$ nondegenerate; symmetric to $C_{\infty}$ ($\chi_{C_{\infty}} = 1$)
- $\{\Pi, \Delta, \Phi\} \equiv E$ doubly degenerate ($\chi_E = 2$)
Mulliken Symbols
Modifying Symbols

With any degeneracy in any centrosymmetric groups:

subscript \( g \) \((\text{gerade})\) symmetric with respect to inversion \((\chi_i > 0)\)

subscript \( u \) \((\text{ungerade})\) antisymmetric with respect to inversion \((\chi_i < 0)\)

With any degeneracy in non-centrosymmetric nonlinear groups:

prime (\( ' \)) symmetric with respect to \( \sigma_h \) \((\chi_{\sigma_h} > 0)\)

double prime (\( '' \)) antisymmetric with respect to \( \sigma_h \) \((\chi_{\sigma_h} < 0)\)

With nondegenerate representations in nonlinear groups:

subscript 1 symmetric with respect to \( C_m \) \((m < n)\) or \( \sigma_v \) \((\chi_{C_m} > 0\) or \(\chi_{\sigma_v} > 0)\)

subscript 2 antisymmetric with respect to \( C_m \) \((m < n)\) or \( \sigma_v \)
\((\chi_{C_m} < 0\) or \(\chi_{\sigma_v} < 0)\)

With nondegenerate representations in linear groups \((C_{\infty v}, D_{\infty h})\):

superscript + symmetric with respect to \( \infty \sigma_v \) or \( \infty C_2 \) \((\chi_{\sigma_v} = 1\) or \(\chi_{C_2} = 1)\)

superscript – antisymmetric with respect to \( \infty \sigma_v \) or \( \infty C_2 \) \((\chi_{\sigma_v} = -1\) or \(\chi_{C_2} = -1)\)