**Equivalence and the Similarity Transformation**

**Equivalence**
- below, Figure 1, is the character table for the $D_{3h}$ point group:

<table>
<thead>
<tr>
<th>$D_{3h}$</th>
<th>E</th>
<th>$2C_3$, $3C_2$, $σ_h$, $2S_3$, $3σ_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1'$</td>
<td>1</td>
<td>1 1 1 1 1 1</td>
</tr>
<tr>
<td>$A_2'$</td>
<td>1</td>
<td>1 -1 1 1 -1</td>
</tr>
<tr>
<td>$E'$</td>
<td>2</td>
<td>-1 0 2 -1 0</td>
</tr>
<tr>
<td>$A_1''$</td>
<td>1</td>
<td>1 1 -1 -1 -1</td>
</tr>
<tr>
<td>$A_2''$</td>
<td>1</td>
<td>1 -1 -1 -1 1</td>
</tr>
</tbody>
</table>

**Figure 1** Character table for $D_{3h}$ point group

- the column headings can represent more than one symmetry operation
  - this could be multiple operations about a single element, or multiple operations about many elements.
  - for example there are three $C_3$ operations associated with the $C_3$ axis for the $D_{3h}$ point group: $C_3^1$, $C_3^2$ and $C_3^3$ (Figure 2)

**Figure 2** The $C_3$ operations

- alternatively there could be three separate elements as in the 3 $C_2$ axes in the $D_{3h}$ point group shown Figure 3, they are labelled $C_2$, $C_2'$, $C_2''$ or alternatively $C_2(a)$, $C_2(b)$ $C_2(c)$ to indicate they are different symmetry elements

**Figure 3** The $3C_2$ axes

- the column headings represent groups of **equivalent operators** within the point group
- these operations have the same type of symmetry element, and the number of equivalent operations in a class is given by "k" in the reduction formula
The equivalent symmetry elements satisfy the similarity transformation:

- if \(a, b\) and \(c\) are elements of a group \(G\) then the elements \(a\) and \(b\) are equivalent if \(a = c^{-1}bc\) (the similarity transformation)
- \(a\) and \(b\) are said to be conjugate
- this relationship is denoted by \(a \sim b\) (\(\sim\) is a tilde)
- another way of writing this relationship which avoids the use of inverses:
  \[
  a = c^{-1}bc \\
  ca = cc^{-1}bc \\
  ca = ebc \quad \text{since} \quad cc^{-1} = e \\
  ca = bc \quad \text{since} \quad eb = b
  \]

- a number of other relationships hold for conjugate elements:
  - \(a \sim a\) (\(a\) is the conjugate of itself)
  - if \(a \sim b\) then \(b \sim a\) (conjugates are symmetric) and if \(a = c^{-1}bc\) then \(b = cac^{-1}\)
  - if \(a \sim b\) and \(b \sim d\) then \(a \sim d\) (conjugates are transitive)

**In Class Problem: Equivalence**

- show that if \(a \sim b\) then \(b \sim a\) by proving \(b = cac^{-1}\)
  
  \[
  a = c^{-1}bc \quad \text{statement of equivalence} \\
  \text{premultiply both sides by } c \\
  \begin{align*}
  ca &= cc^{-1}bc \\
  \text{and} \quad c^{-1}c &= cc^{-1} = e
  \end{align*} \\
  c^{-1} = bc \\
  \begin{align*}
  &\text{and} \quad c^{-1}c = cc^{-1} = e \quad \text{and} \quad ec = c \\
  &\text{ca = ebc} \\
  &\text{and} \quad ec = c \\
  &\text{thus} \quad b = cac^{-1}
  \end{align*}
  \]

- the equivalent members of a group form an equivalence class or a conjugate class or just a "class"
- all the members of a group can be partitioned into non-overlapping subsets that are conjugate classes
- only operations of the same type can form a class
- \(e\) always forms a class on its own since for any element \(a \in G\)
- the elements of a cyclic group are always equivalent

![Figure 4 The 3C axes](image-url)
the number of elements in a class is given by "k" in the reduction formula you used last year.
the number of elements in a class is the coefficient to the symmetry element in the row headings of the character tables.

- Abelian groups have only classes with a single element:
  \[ a = c^{-1}bc \quad \text{statement of equivalence} \]
  \[ \text{since} \quad bc = cb \quad (\text{abelian groups commute}) \]
  \[ a = c^{-1}cb \]
  \[ \text{and} \quad c^{-1}c = e \]
  \[ a = b \]

- For example consider the D_3 group where the equivalence classes are:
  \[ C_E = \{ E \} \]
  \[ C_{c_1} = \{ C_3, C_3^{-1} \} \]
  \[ C_{c_2} = \{ C_2(a), C_2(b), C_2(c) \} \]

- An example of some equivalence relations are shown below

Figure 5

- The C_2 operations form an equivalence class such that \( a = c^{-1}bc \) where a and b are \( C_{c_2} = \{ C_2(a), C_2(b), C_2(c) \} \) and c is \( \{ E \} \) or \( \{ C_3, C_3^{-1} \} \)
for example we can show that $[C_3]^{-1}C_2(a)C_3 = C_2(c)$ and thus that $C_2(a) \sim C_2(c)$ using diagrams:

define co-ordinate system and symmetry elements

depict the operations starting from the right

- Consider the two distinct $C_3$ operations: $C_3^1$ and $C_3^2 = C_3^{-1}$
  - the $C_3$ and $C_{3h}$ point groups are Abelian and each operation belongs to its own class including $C_3^1$ and $C_3^2$  
  - however for the $C_{3v}$, $D_3$, $D_{3h}$ and $D_{3d}$ point groups these two operations belong to the same class and are equivalent.

Figure 6
In Class Problem: Equivalence Relationships

- show the equivalence relationship \([C_3]^{-1}C_2(c)C_3 = C_2(b)\) using diagrams

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\quad
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1/2 & -\sqrt{3}/2 \\
0 & \sqrt{3}/2 & -1/2
\end{bmatrix}
\quad
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1/2 & \sqrt{3}/2 \\
0 & -\sqrt{3}/2 & -1/2
\end{bmatrix}
\]

\[
D(E)
\quad D(C_3)
\quad D(C_3^{-1})
\]

\[
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1/2 & -\sqrt{3}/2 \\
0 & -\sqrt{3}/2 & 1/2
\end{bmatrix}
\quad
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1/2 & \sqrt{3}/2 \\
0 & \sqrt{3}/2 & 1/2
\end{bmatrix}
\quad
\begin{bmatrix}
-1 & 0 & 0 \\
0 & -1/2 & -\sqrt{3}/2 \\
0 & -\sqrt{3}/2 & 1/2
\end{bmatrix}
\]

\[
D(C_2(a))
\quad D(C_2(b))
\quad D(C_2(c))
\]

- the equivalence relationship must also hold for matrices: symmetry operators that are equivalent will have matrix representations that are equivalent:
  - if \(a\sim b\), ie \(a = c^{-1}bc\) then \(A\sim B\), ie \(D(A) = [D(C)]^{-1}D(B)D(C)\) where \(D(A), D(B),\) and \(D(C)\) are matrix representations of \(a, b\) and \(c\)
  - symmetry operators that are equivalent, have matrices that are equivalent, and the same relationships are obeyed:
    \[
    D(A) = D(C^{-1}BC)
    = D(C^{-1})D(B)D(C)
    = [D(C)]^{-1}D(B)D(C)
    \]
  - the last line holds because for a homomorphism \(f(a^{-1}) = [f(a)]^{-1}\)
  - equivalence collects specific operations and thus matrix representations of those operators together in a class,
    \[
    a = c^{-1}bc \quad \forall a, b, c \in G
    \]
    \[
    A = C^{-1}BC \quad \forall A, B, C \in G'
    \]
In Class Problem: Equivalence Relationships

- we have shown using diagrams that $[C_3]^{-1} C_3(a)C_3 = C_2(c)$ now do the same using matrices:

$$D(C_3) = \begin{pmatrix} +1 & 0 & 0 \\ 0 & -1/2 & -\sqrt{3}/2 \\ 0 & \sqrt{3}/2 & -1/2 \end{pmatrix}, \quad D(C_3^{-1}) = \begin{pmatrix} +1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & -1/2 \end{pmatrix}, \quad D(C_2(a)) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Characters

- characters are the numbers inside the character table
- equivalent operations (operations in the same class) have the same character (outline justification of this statement is included in the problems document)
- characters are the trace of a matrix representation of an operator, where the trace is the sum of the diagonal elements of the matrix

$$trace(D(R)) = \sum_i D_{ii}(R) = \chi(R)$$

$$A = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{32} & a_{32} & a_{33} \end{bmatrix} \quad \chi(A) = \sum_i a_{ii} = a_{11} + a_{22} + a_{33}$$

- additional requirement of the matrices we will be dealing with is that they are Unitary
  - this requires that the inverse be equal to the complex conjugate transpose ($A^{-1} = A^\dagger$)
  - the complex conjugate transpose = adjoint of a matrix and is represented as ($A^\dagger$)
  - the complex conjugate ($A^*$) you have met before when studying complex numbers, if $z=x+iy$ then the complex conjugate is $z^*=x-iy$
  - the transpose of a matrix ($A^t$) exchanges all rows and columns, ie $a_{ij}$ becomes $a_{ji}$
  - if the matrix elements are real then $A^\dagger = A^t$
  - and thus $A^{-1} = A^*=A^t$

$$A = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{32} & a_{32} & a_{33} \end{bmatrix}, \quad A^*=\begin{bmatrix} a_{11}^* & a_{21}^* & a_{31}^* \\ a_{12}^* & a_{22}^* & a_{32}^* \\ a_{13}^* & a_{23}^* & a_{33}^* \end{bmatrix}, \quad A^t = \begin{bmatrix} a_{11} & a_{21} & a_{31} \\ a_{12} & a_{22} & a_{32} \\ a_{13} & a_{23} & a_{33} \end{bmatrix}$$
proof that the matrices of equivalent operations have the same character

\[ B = C^{-1}AC \]

require \( C^{-1} = C^\dagger \)

matrix is real: \( C^{-1} = C^\dagger = C^t \)

\[
\begin{pmatrix}
  b_{11} & b_{12} \\
  b_{21} & b_{22}
\end{pmatrix}
= \begin{pmatrix}
  c_{11} & c_{21} \\
  c_{12} & c_{22}
\end{pmatrix}
\begin{pmatrix}
  a_{11} & a_{12} \\
  a_{21} & a_{22}
\end{pmatrix}
\begin{pmatrix}
  c_{11} & c_{12} \\
  c_{21} & c_{22}
\end{pmatrix}
= \begin{pmatrix}
  c_{11} & c_{21} \\
  c_{12} & c_{22}
\end{pmatrix}
\begin{pmatrix}
  (a_{11}c_{11} + a_{12}c_{21}) & (a_{11}c_{12} + a_{12}c_{22}) \\
  (a_{21}c_{11} + a_{22}c_{21}) & (a_{21}c_{12} + a_{22}c_{22})
\end{pmatrix}
= \begin{pmatrix}
  [b_{11}] & [X] \\
  [X] & [b_{22}]
\end{pmatrix}
\]

\[
\begin{align*}
    b_{11} &= [c_{11}(a_{11}c_{11} + a_{12}c_{21}) + c_{21}(a_{21}c_{11} + a_{22}c_{21})] \\
    b_{22} &= [c_{12}(a_{11}c_{12} + a_{12}c_{22}) + c_{22}(a_{21}c_{12} + a_{22}c_{22})]
\end{align*}
\]

consider one element:

\[
    b_{11} = c_{11}(a_{11}c_{11} + a_{12}c_{21}) + c_{21}(a_{21}c_{11} + a_{22}c_{21})
\]

\[
    = c_{11}a_{11}c_{11} + c_{11}a_{12}c_{21} + c_{21}a_{21}c_{11} + c_{21}a_{22}c_{21}
\]

\[
    = \sum_{j,k} c_{k1} a_{jk} c_{kj}
\]

\[
    = \sum_{j,k} a_{jk} c_{kj}
\]

\[
    = \sum_{j,k} a_{jk} \delta_{ij} \delta_{ki}
\]

\[
    = a_{11}
\]

therefore in general:

\[
    \sum_i b_{ii} = \sum_{i,j,k} a_{jk} c_{ij}^t c_{ki}
\]

but \( C^\dagger C = I \) therefore \( \sum_{i,j,k} c_{ij}^t c_{ki} = \delta_{ij} \delta_{ki} \)

\[
    = \sum_i a_{ii}
\]

• (comment: \( \delta_{ij} \) means that the answer is 0 if \( i \neq j \) and 1 if \( i=j \), the first delta requires \( j=i \) for a non-zero answer, and the second therefore requires \( k=j=i \) for a non-zero answer.)

• thus \( B \) and \( A \) have the same trace, and the same character

• previously we have compared several matrix representations for the symmetry elements of the \( D_3 \) point group
  o notice that the trace of matrices representing symmetry elements in the same class are the same
\[ \chi(C^3_1) = \text{trace} \begin{pmatrix} -\frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} \end{pmatrix} = -\frac{1}{2} + -\frac{1}{2} = -1 \]

\[ \chi(C^1_3) = \text{trace} \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} = +\frac{1}{2} - \frac{1}{2} = 0 \]

Thus in general:

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
D_3 & E & C^1_3(z) & C^{-1}_3(z) & C^1_3(a) & C^1_3(b) & C^1_3(c) \\
\hline
B(s) & 1 & 1 & 1 & 1 & 1 & 1 \\
B(p_x) & 1 & 1 & 1 & -1 & -1 & -1 \\
B(p_x, p_y) & 2 & -1 & -1 & 0 & 0 & 0 \\
\hline
\end{array}
\]

The character table for \( D_3 \) becomes:

\[
\begin{array}{|c|c|c|c|}
\hline
D_3 & E & 2C_3 & 3C_2 \\
\hline
A_1 & 1 & 1 & 1 \\
B_1 & 1 & 1 & -1 \\
E & 2 & -1 & 0 \\
\hline
\end{array}
\]

- Thus given any equivalent matrices (or operators) we only need to work out the trace or character for one matrix in that class to know the character for all the other operators in that class.
- Turning this statement around: the character of a symmetry operator is unaffected by changes the matrix representation of that operator.
- This means that we can choose any reasonable basis and determine the character for the symmetry operation.
- Key point: the trace or character is dependent only on the symmetry and not on the particular chemical system being studied.
- In addition matrices/operators related by a similarity transformation (\( A \sim B \)) have
  - the same determinant
  - the same eigenvalues
  - a common set of eigenvectors
we know that the energy of a molecule does not change under a symmetry operation, more specifically the Hamiltonian is invariant under a symmetry operation $R \cdot (RH) = H$

symmetry operators and $H$ commute, and are conjugate

$$RH = HR$$

$$R^{-1}RH = R^{-1}HR$$

$$H = R^{-1}HR$$

thus the symmetry operator and the Hamiltonian can have the same eigenfunctions

- this is why we could use symmetry arguments to obtain the symmetry adapted MOs last year
- this is why we can use the eigenfunctions of rotational symmetry as solutions to the angular part of the Schrödinger equation

**Transformation Matrices**

- a much deeper and more general relationship can be deduced from the equivalence relationship.
- we know that for $A$, $B$ and $C$ all elements of the same group that $B = C^{-1}AC$
- now let us consider a more general case where $C$ is not necessarily an element of the group. To differentiate between a matrix that represents an element of the group and a more general matrix we use $T$ to represent the more general matrix.
- $T$ is known as a **transformation matrix**. $A' = TAT^{-1}$ were $A$ is transformed into $A'$ by operation of the transformation matrix, $T$.
  - for example when a matrix is diagonalised we have transformed it
- we require that $T$ be a unitary matrix ie that $T^{-1} = T^\dagger$, and thus where the matrix is real that $T^{-1} = T^\dagger = T^t$ which results in $T^{-1}T = T^\dagger T = I$.
- transformation matrices convert both vectors and operators from one representation into another. Thus they effect both the coefficient and the basis part of the vector or operator expression.
  - for example if a cartesian vector is represented by the coefficient vector $(x \ y \ z)^t$ and the basis vector is $(\hat{i} \ \hat{j} \ \hat{k})$:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = x\hat{i} + y\hat{j} + z\hat{k}$$

- the transformation matrix works as:
\[
\begin{pmatrix}
\hat{i} & \hat{j} & \hat{k}
\end{pmatrix}
T^\dagger T
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
= x\hat{i}' + y\hat{j}' + z\hat{k}'
\]

\[
\begin{pmatrix}
\hat{i} & \hat{j} & \hat{k}
\end{pmatrix}T^\dagger = \begin{pmatrix}
\hat{i}' & \hat{j}' & \hat{k}'
\end{pmatrix}
\text{and}
T
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
= \begin{pmatrix}
x' \\
y' \\
z'
\end{pmatrix}
\]

\[
\begin{pmatrix}
\hat{i}' & \hat{j}' & \hat{k}'
\end{pmatrix}
\begin{pmatrix}
x' \\
y' \\
z'
\end{pmatrix}
= x\hat{i}' + y\hat{j}' + z\hat{k}'
\]

(note: where there is a dagger (\(\dagger\)), the matrix operates to the left)

- thus a new coefficient vector \(\begin{pmatrix} x' & y' & z' \end{pmatrix}^T\) and a new basis vector \(\begin{pmatrix} \hat{i}' & \hat{j}' & \hat{k}' \end{pmatrix}\) have been generated.
- thus if \(D(R)\) is the matrix representation of \(R\) in the basis \(\begin{pmatrix} \hat{i} & \hat{j} & \hat{k} \end{pmatrix}\), then \(TD(R)T^\dagger\) is the matrix representation of \(R\) in the basis \(\begin{pmatrix} \hat{i}' & \hat{j}' & \hat{k}' \end{pmatrix}\) and \(D'(R)\) and \(D(R)\) represent the same symmetry operation, \(R\)
- because the equivalence relationship \(A' = T^{-1}AT\) still holds for any unitary transformation matrix \(T\) the trace\((A')\)=trace\((A)\) and the character of the matrix is independent of the basis!
- this means that we can choose any reasonable basis and determine the character for the symmetry operation

**key point:** the trace or character is dependent only on the symmetry and not on the particular chemical system being studied

- matrices related by a similarity transformation have
  - the same determinant \(\text{det}(D(A))=\text{det}(D(B))\)
  - the same eigenvalues \(\lambda(A)=\lambda(B)\)
  - the same trace \(\chi(A)=\chi(B)\)

**key point:** the determinant and eigenvalues of matrices related by a unitary transformation are the same.

**Key Points**

- to be able to describe equivalence, and define what is meant by a "class" in group theory
- be able to show using both diagrams and matrix mechanics when two symmetry elements are equivalent
- be able to express the equivalence relationship for operators and matrices
- be able to use the commutator and equivalence relationships in proofs
- be able to explain what a character is
• be able to describe why transformation matrices related by a similarity transformation are so important

**Problems**

• Find the equivalence classes of $D_{4h}$. Explain how you would verify that the $C_2$ operations belong to different classes.

• show using diagrams that \[
\begin{bmatrix}
C_2(a) \end{bmatrix}^{-1} C_3 C_2(a) = \begin{bmatrix} C_3 \end{bmatrix}^{-1}
\]

• show using matrices that \[
\begin{bmatrix} C_3 \end{bmatrix}^{-1} C_2(b) C_3 = C_2(a)
\]

• show that \[
C_3 C_2(a) \begin{bmatrix} C_3 \end{bmatrix}^{-1} = C_2(b)
\]

**Answers**

• Find the equivalence classes of $D_{4h}$. Explain how you would verify that the $C_2$ operations belong to different classes.

\[
D_{4h} = \{ E, 2C_4, C_2, 2C_2', 2C_2'', i, 2S_4, \sigma_h, 2\sigma_v, 2\sigma_d \}
\]

\[
C_4, C_2
\]

\[
\sigma_{v}(yz) \quad \sigma_{v}(xz)
\]

\[
C_2'(x) \quad C_2'(y) \quad C_2'(z)
\]

from above

\[
C_2''(b) \quad C_2''(a)
\]

\[
\sigma_{d}(b) \quad \sigma_{d}(a)
\]

o equivalence classes are:

\[
\begin{align*}
\{E\} & , \{C_4 \} \{C_4^{-1}\} , \{C_2 \} \{C_2^{-1}\} , \{C_2'(x) \} \{C_2'(y)\} , \{C_2''(a) \} \{C_2''(b)\} , \\
\{i\} & , \{S_4 \} \{S_4^{-1}\} , \{\sigma_h \} \{\sigma_h^{-1}\} , \{\sigma_{v}(xz) \} \{\sigma_{v}(yz)\} , \{\sigma_{d}(a) \} \{\sigma_{d}(b)\} \\
\end{align*}
\]

o to be in the same class \(a = c^{-1}bc\), thus to show that the $C_2$ operations are not in the same class, we have to show that no other symmetry operation will link two $C_2$ operations from different classes together, ie we have to show that \(a \neq c^{-1}bc\) for \(a=C_2\) and \(b=\) both \(C_2'\) and \(C_2''\) and \(c=\) every other element in the group

\[
a^{-1} C_2 a \neq C_2'(x) \neq C_2'(y) \neq C_2''(a) \neq C_2''(b)
\]

\[
a = E, C_4', C_4^{-1}, i, S_4', S_4^{-1}, \sigma_{v}(xz), \sigma_{v}(yz), \sigma_{d}(a), \sigma_{d}(b)
\]

\[
= C_2'(x), C_2'(y), C_2''(a), C_2''(b)
\]

• show that \[
C_3 C_2(a) \begin{bmatrix} C_3 \end{bmatrix}^{-1} = C_2(b)
\]
$[C_3]^{-1}$

$C_3(a)$

$C_3$

$C_2(b)$

$C_2 C_3(a)[C_3]^{-1} = C_3(b)$