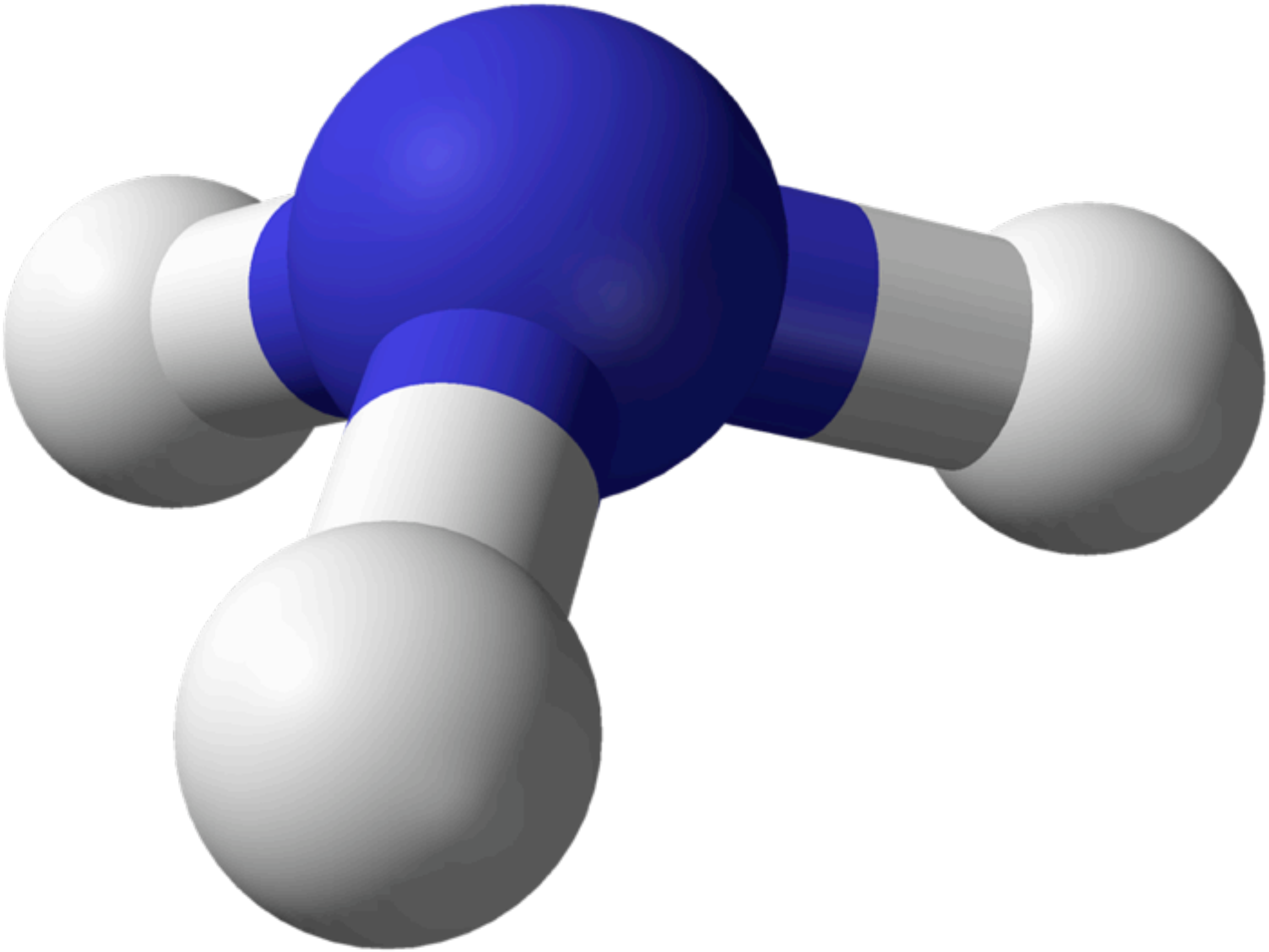
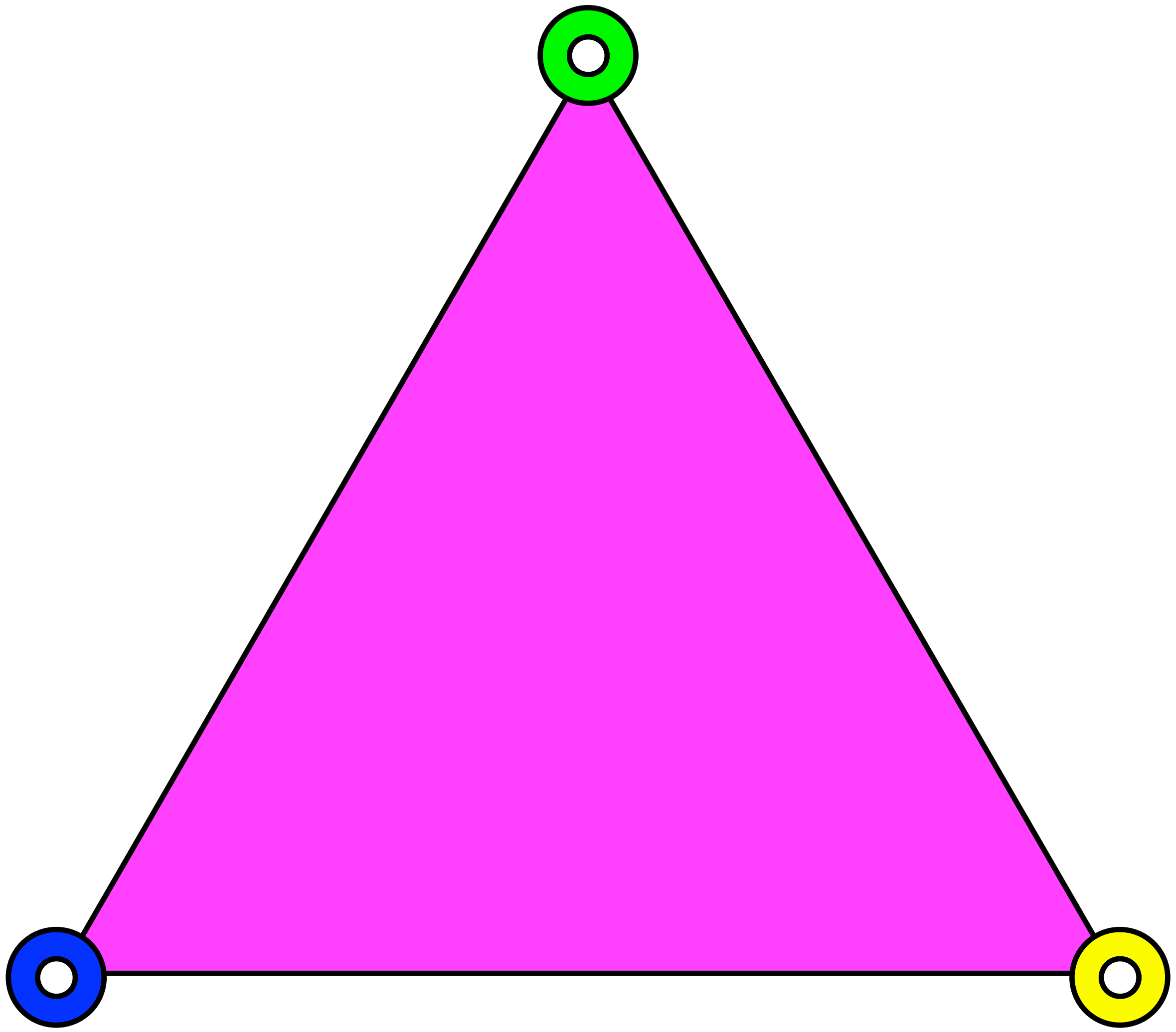
Introduction to group theory

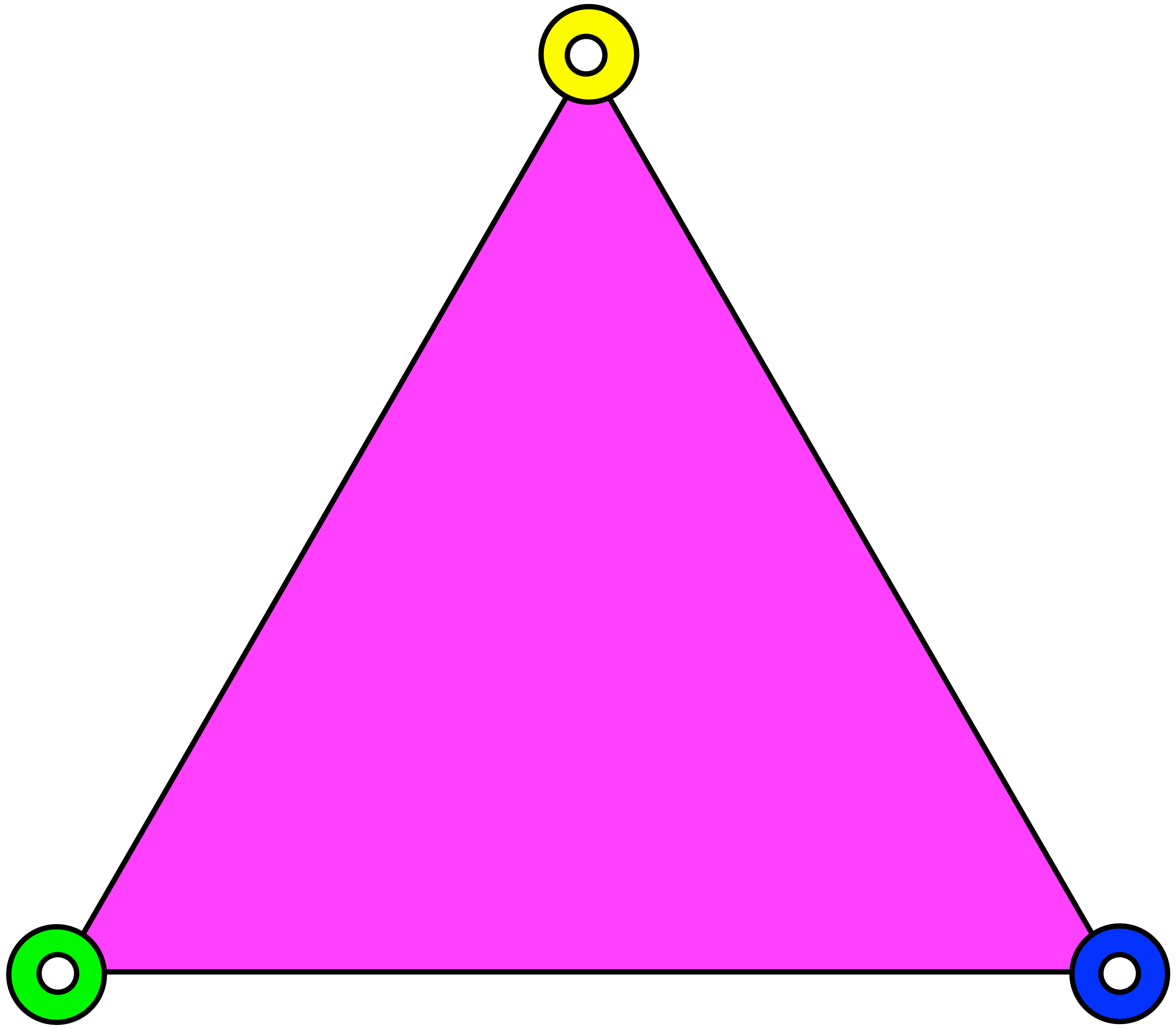
Symmetry operations of the ammonia molecule



Symmetry operations of the equilateral triangle

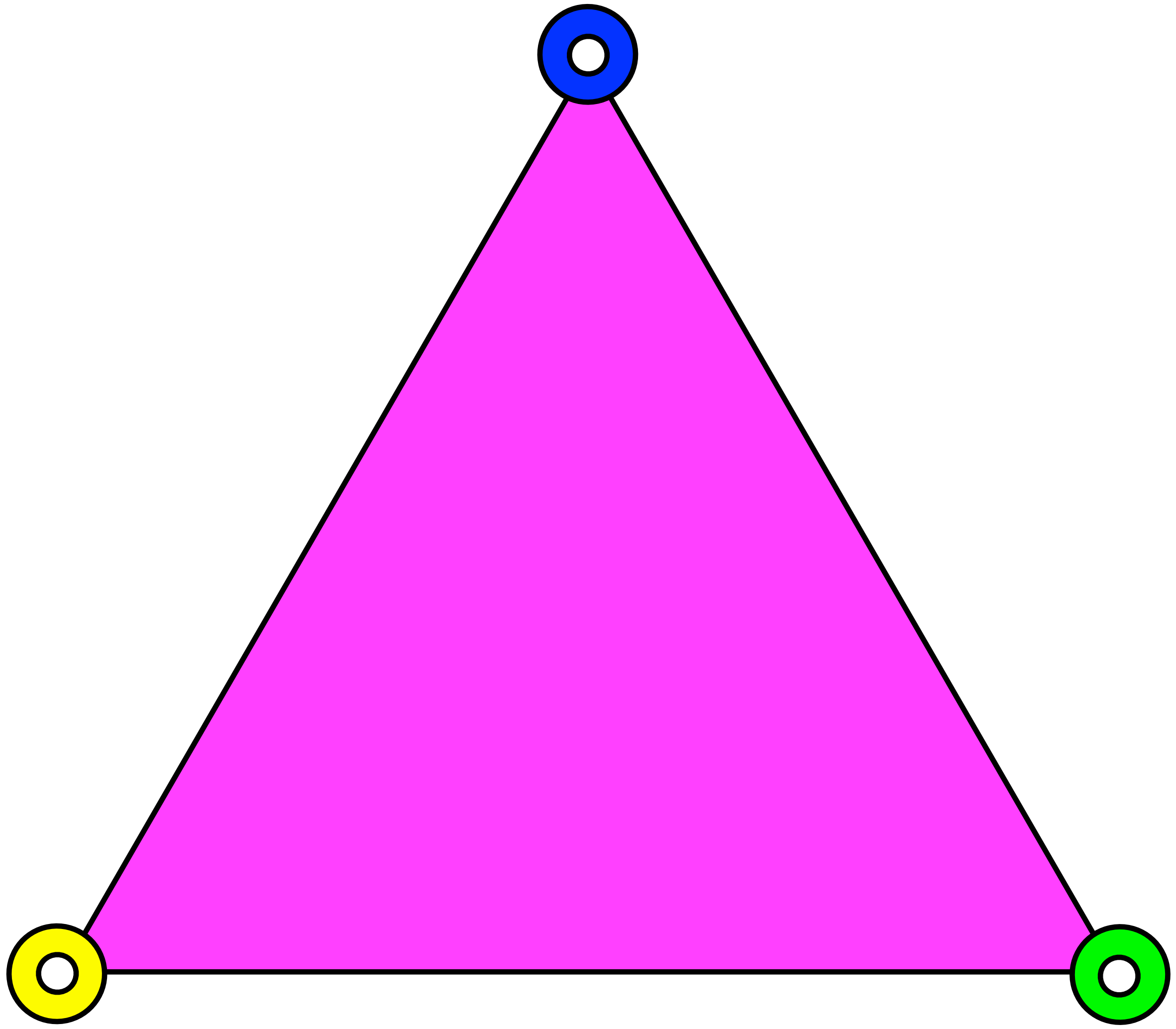


Rotation by 2π/3 around the center



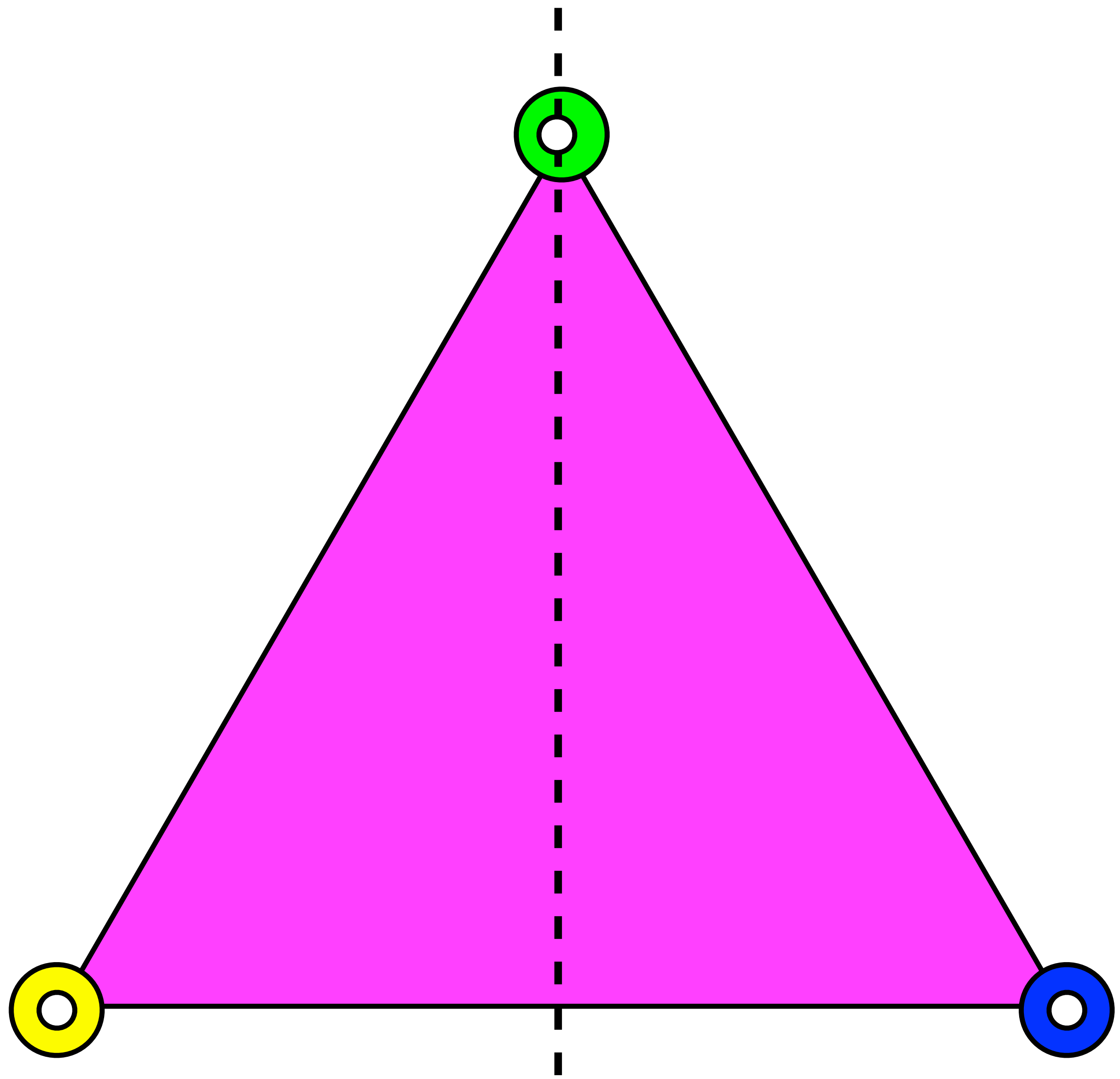
$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

Rotation by 2*2π/3 around the center



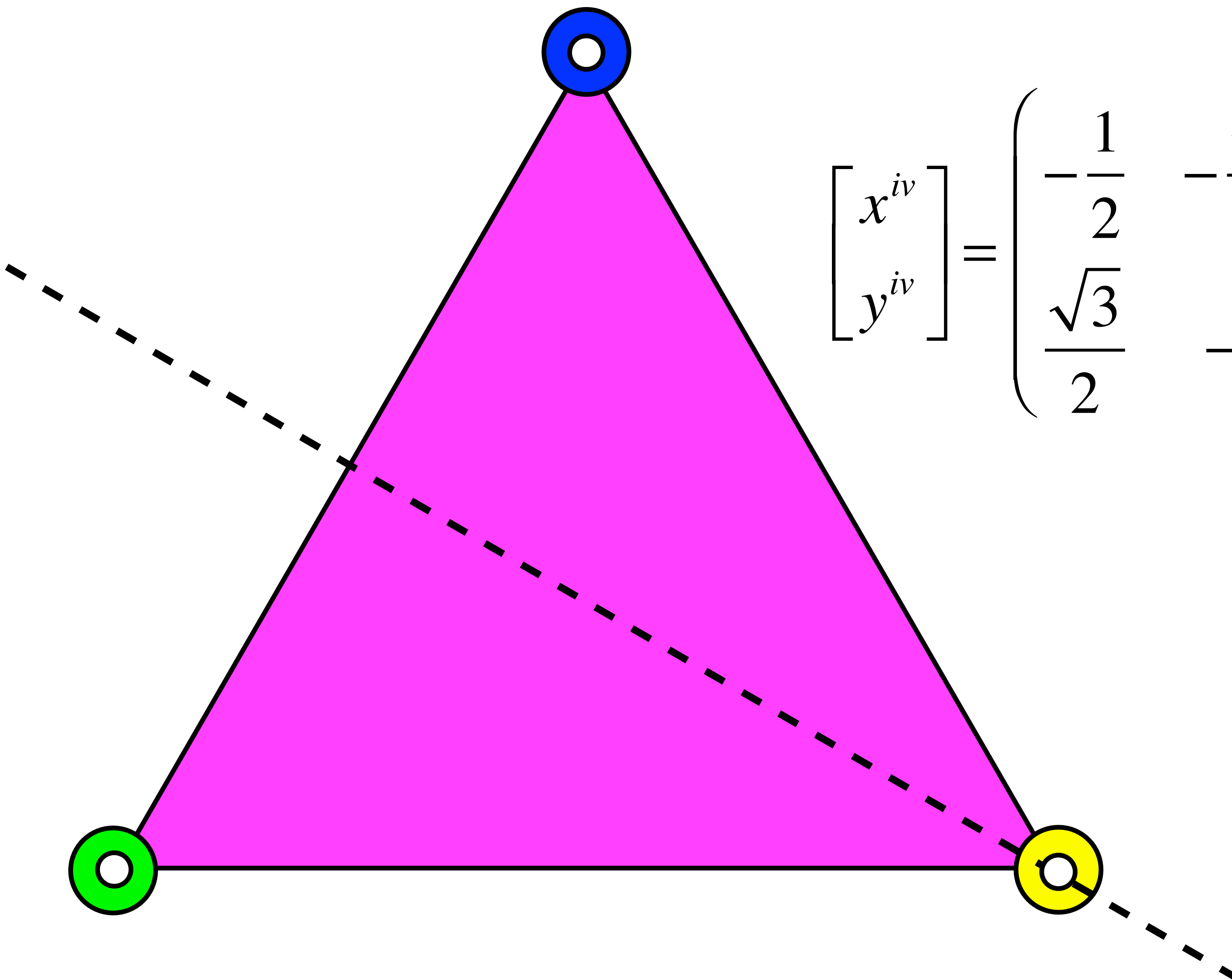
$$\begin{bmatrix} x'' \\ y'' \end{bmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

Reflection about the yz plane



$$\begin{bmatrix} x''' \\ y''' \end{bmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

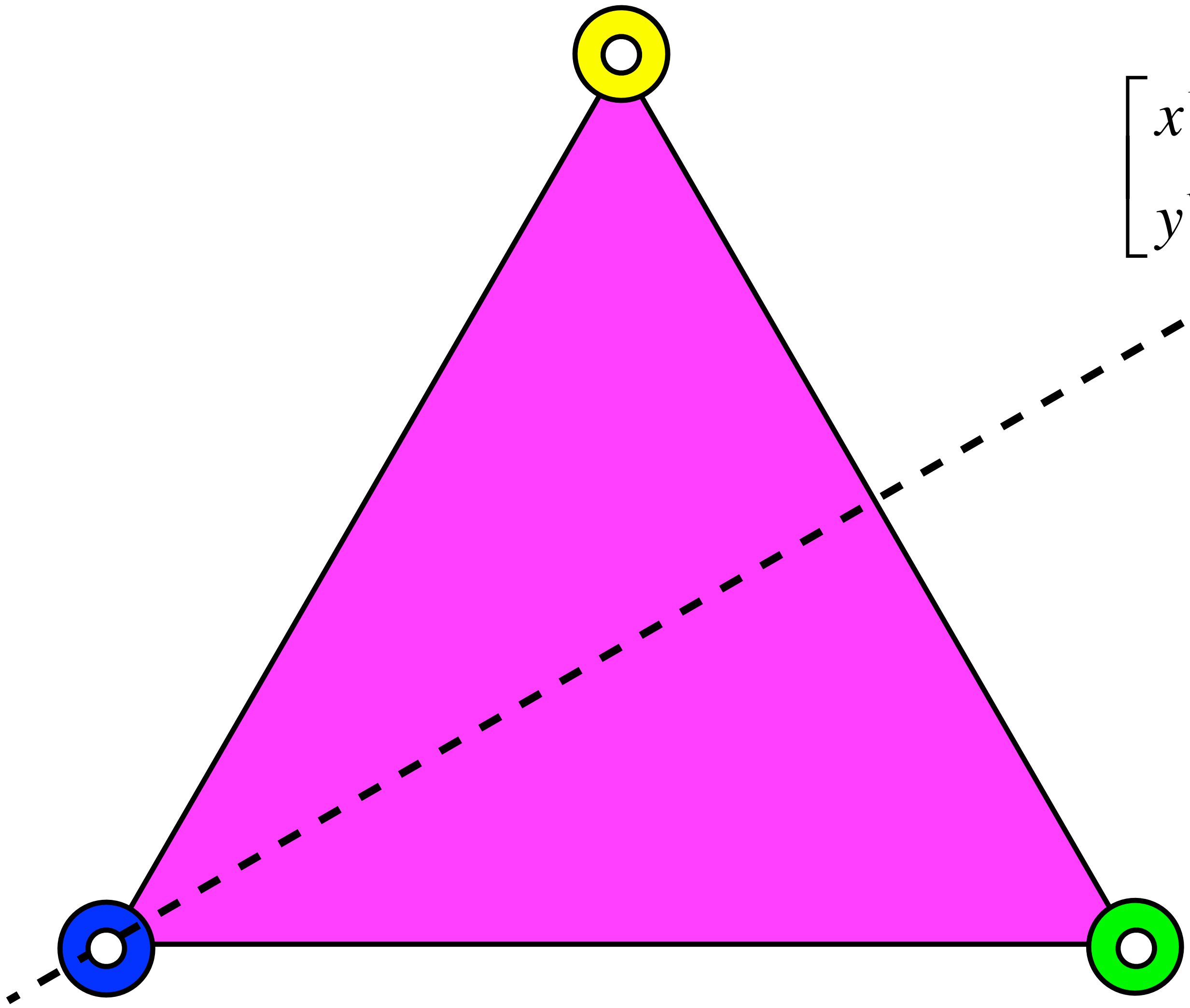
Reflection about the yz plane followed by a rotation by 2π/3 around the center



$$\begin{bmatrix} x^{iv} \\ y^{iv} \end{bmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

Equivalent to a single reflection operation!

Rotation by 2π/3 around the center followed by a reflection by about the yz plane



$$\begin{bmatrix} x^v \\ y^v \end{bmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

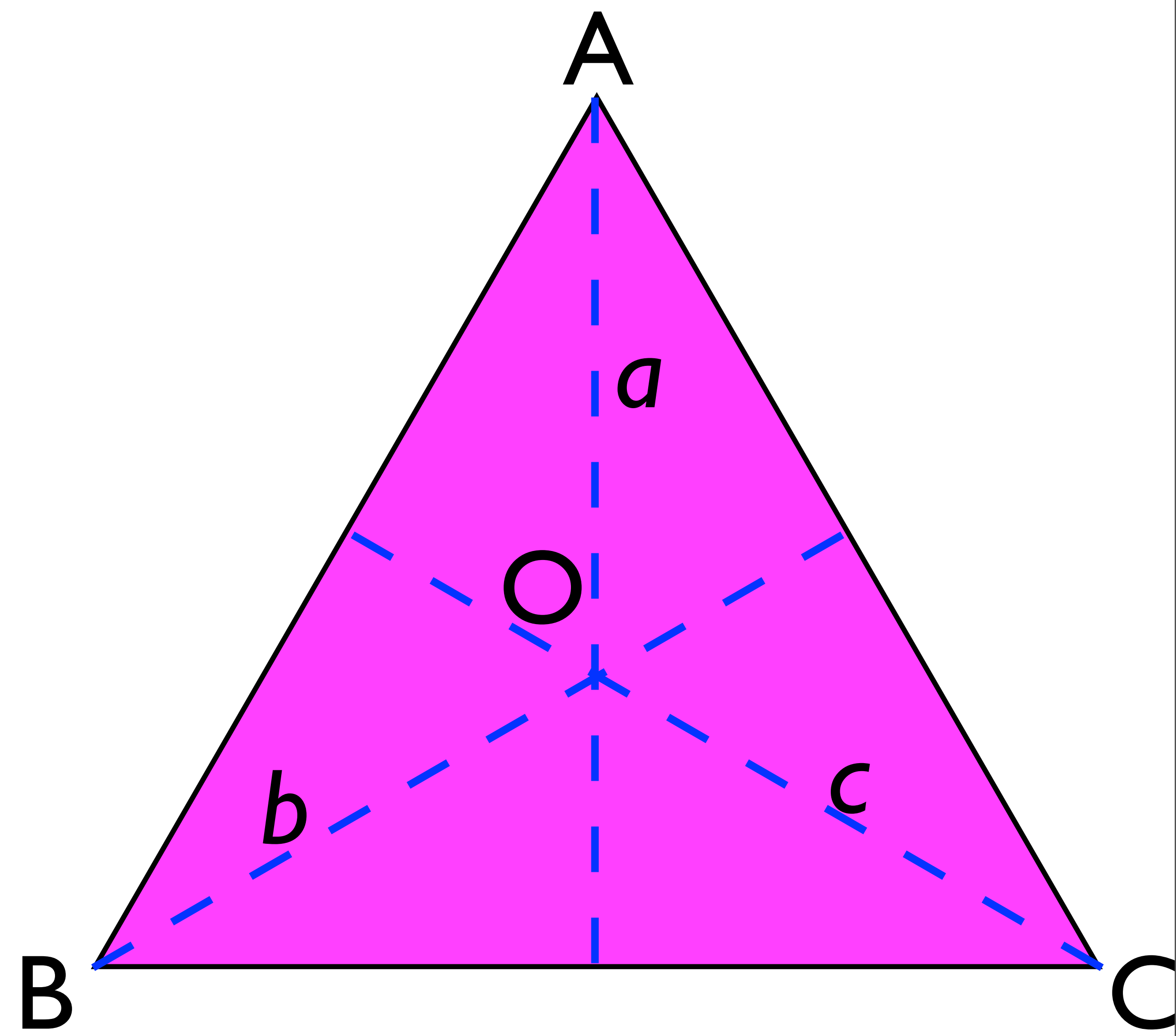
Equivalent to ***a different*** single reflection operation!

Definition of groups

A collection of elements A, B, C, . . . form a group when

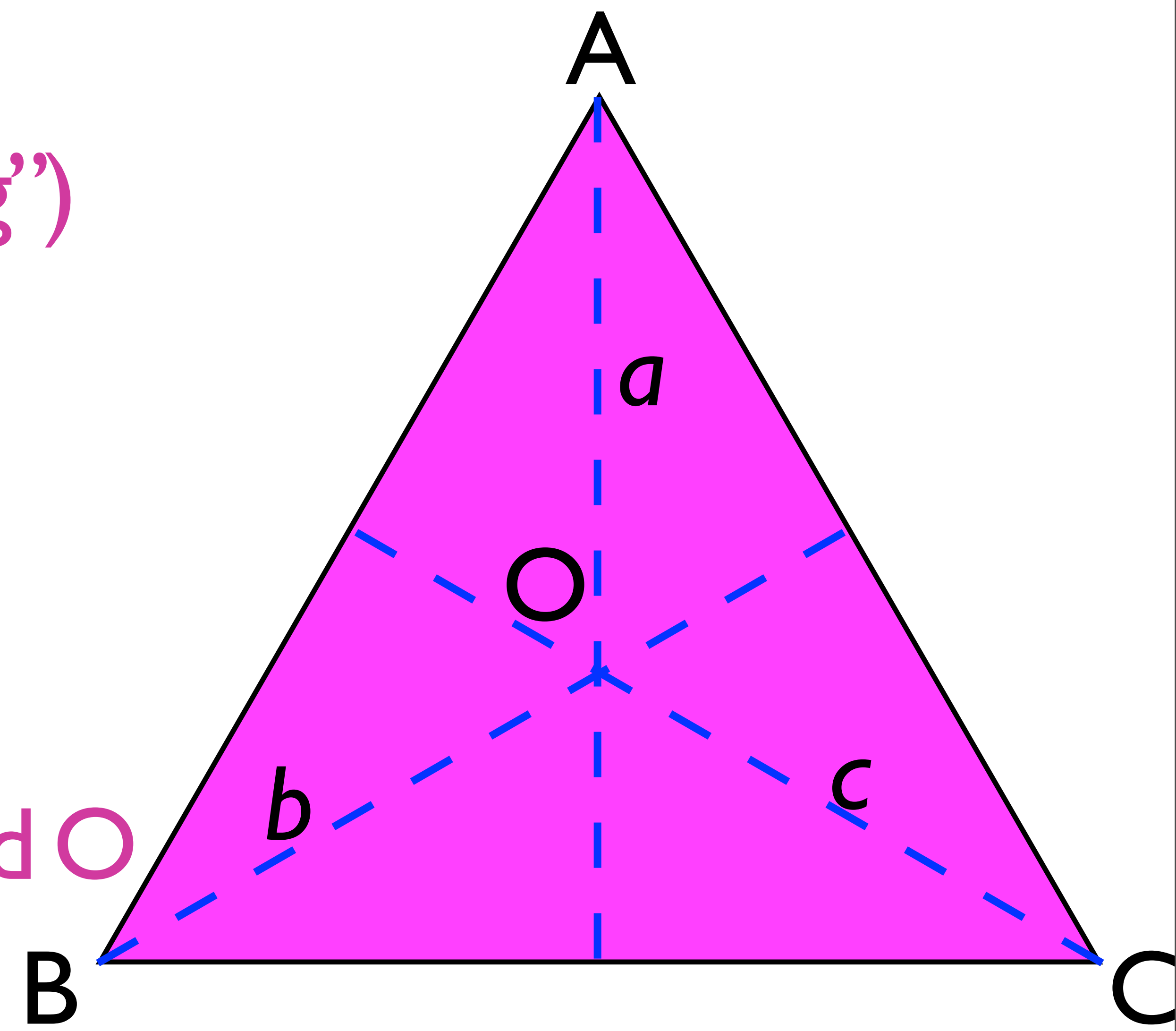
1. The product of any two elements of the group is itself an element of the group. For example, relations of the type AB = C are valid for all members of the group.
2. The associative law is valid – i.e., (AB)C = A(BC).
3. There exists a unit element E (also called the identity element) such that the product of E with any group element leaves that element unchanged AE = EA = A.
4. For every element there exists an inverse, $A^{-1} A = AA^{-1} = E$.

The 6 symmetry operations of the equilateral triangle:



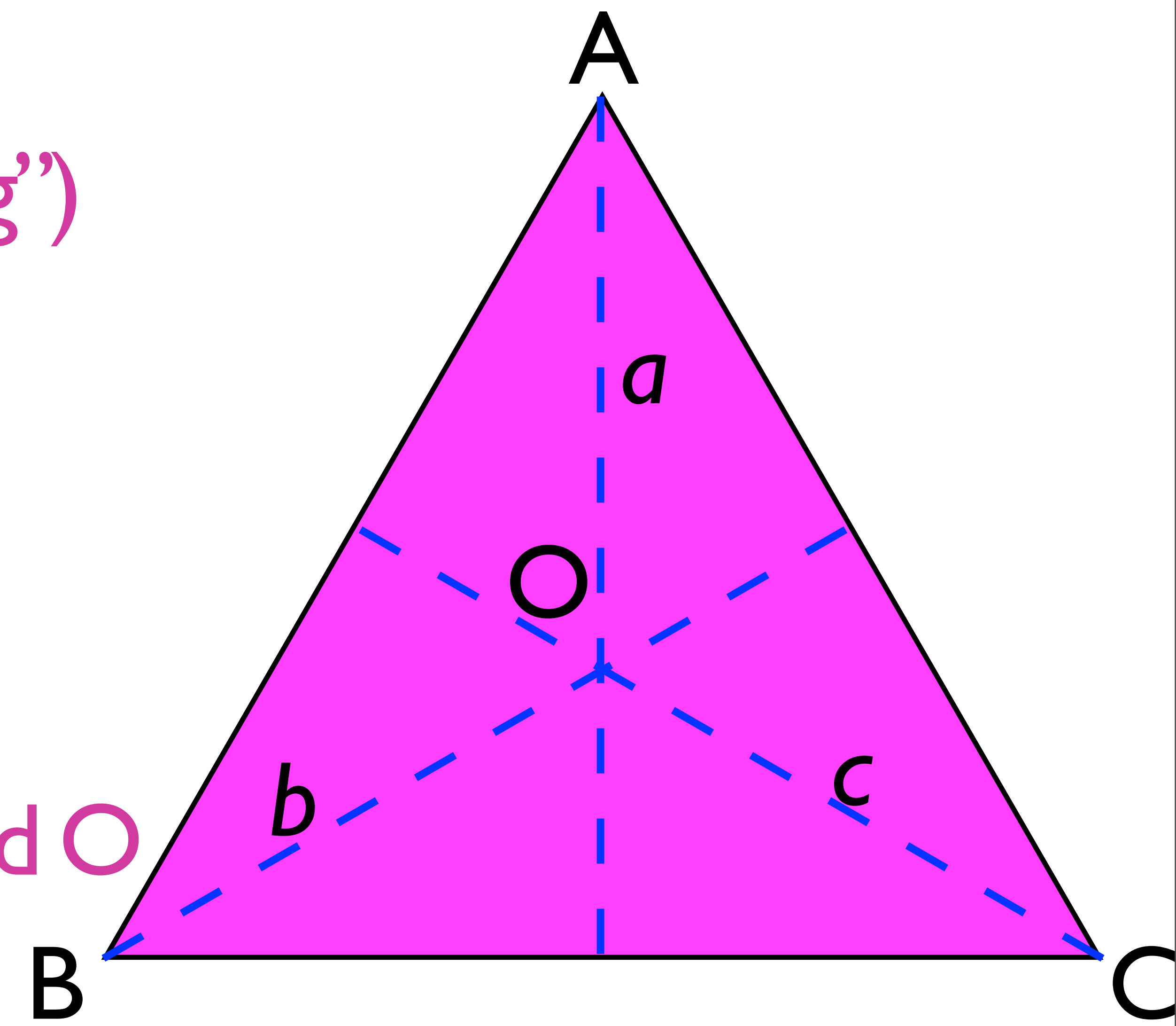
The 6 symmetry operations of the equilateral triangle:

E) The identity operation ("do nothing")
A) Mirroring about *a*
B) Mirroring about *b*
C) Mirroring about *c*
D) Rotation by 2π/3 around O
F) Rotation by 4π/3 (or -2π/3) around O

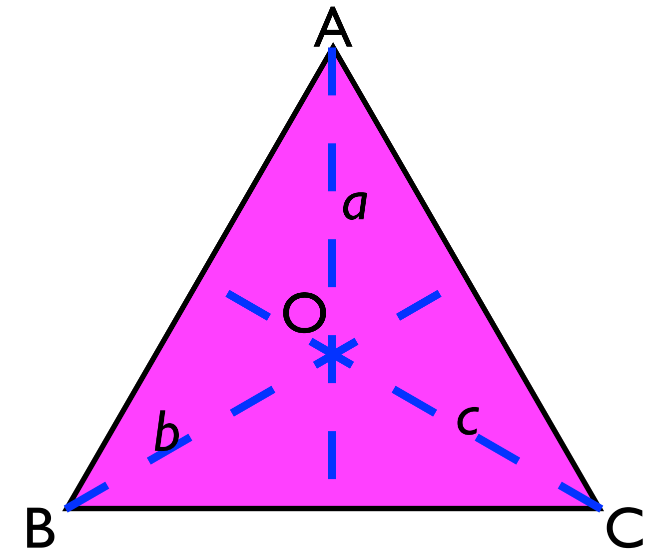


The 6 symmetry operations of the equilateral triangle:

E) The identity operation ("do nothing")
A) Mirroring about *a*
B) Mirroring about *b*
C) Mirroring about *c*
D) Rotation by 2π/3 around O
F) Rotation by 4π/3 (or -2π/3) around O



Form a group (C_{3v})


A
a
O
b
c
B
C

E) The identity operation ("do nothing")

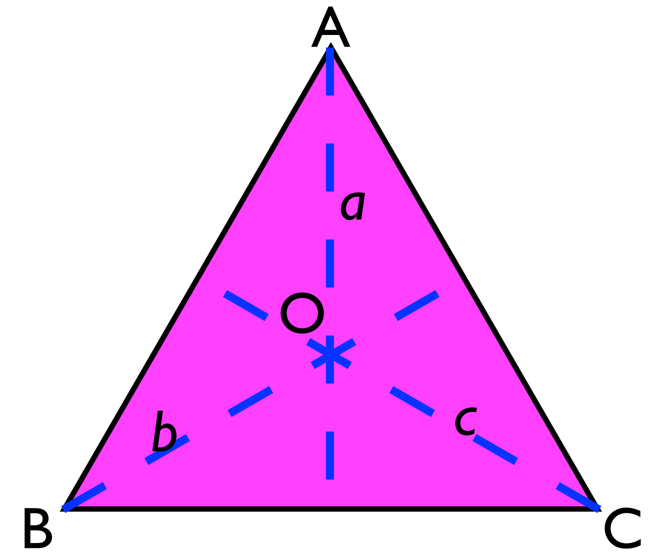
A) Mirroring about *a*

B) Mirroring about *b*

C) Mirroring about *c*

D) Rotation by 2π/3 around O

F) Rotation by 4π/3 (or -2π/3) around O



E) The identity operation ("do nothing")

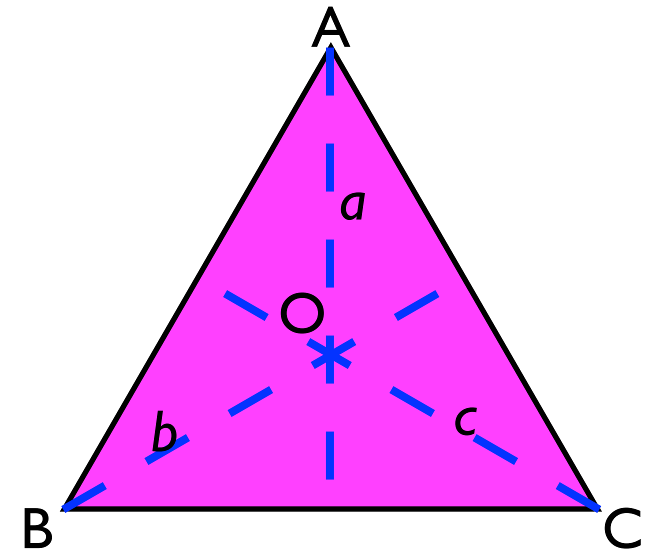
A) Mirroring about *a*

B) Mirroring about *b*

C) Mirroring about *c*

D) Rotation by 2π/3 around O

F) Rotation by 4π/3 (or -2π/3) around O



We can set up a multiplication table for the group C_{3v}:

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

Subgroups

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

Subgroups

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

Subgroups

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

	E	B
E	E	B
B	B	E

Subgroups

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

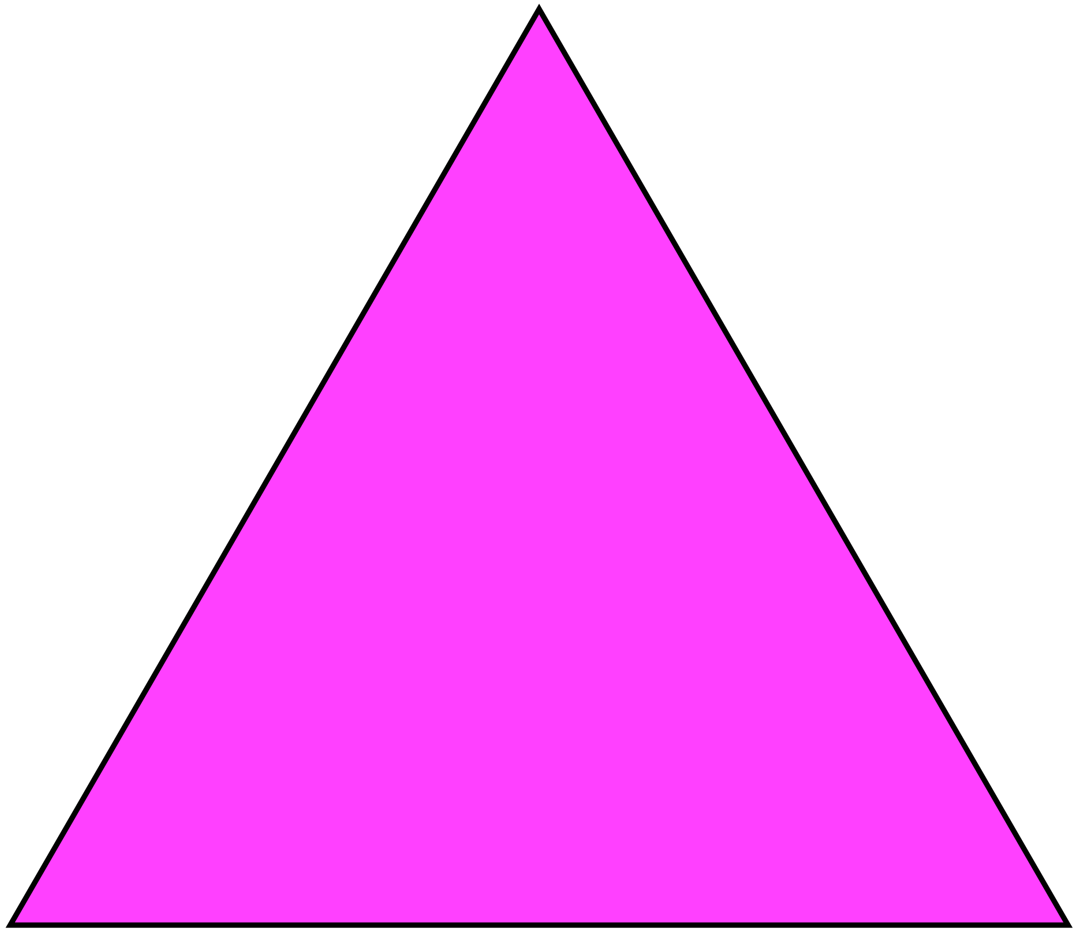
	E	C
E	E	C
C	C	E

Subgroups

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

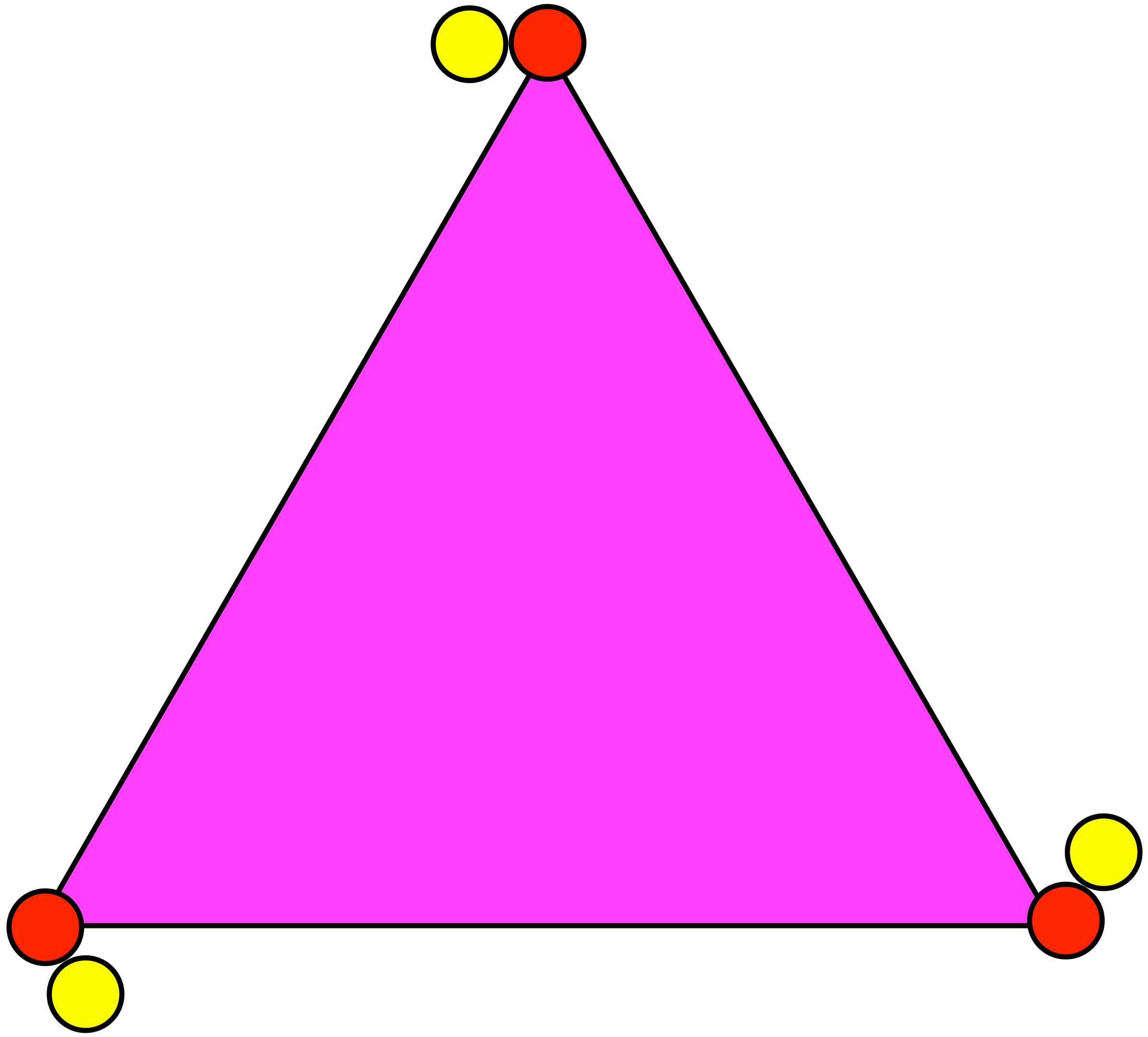
	E	D	F
E	E	D	F
D	D	F	E
F	F	E	D

Subgroups



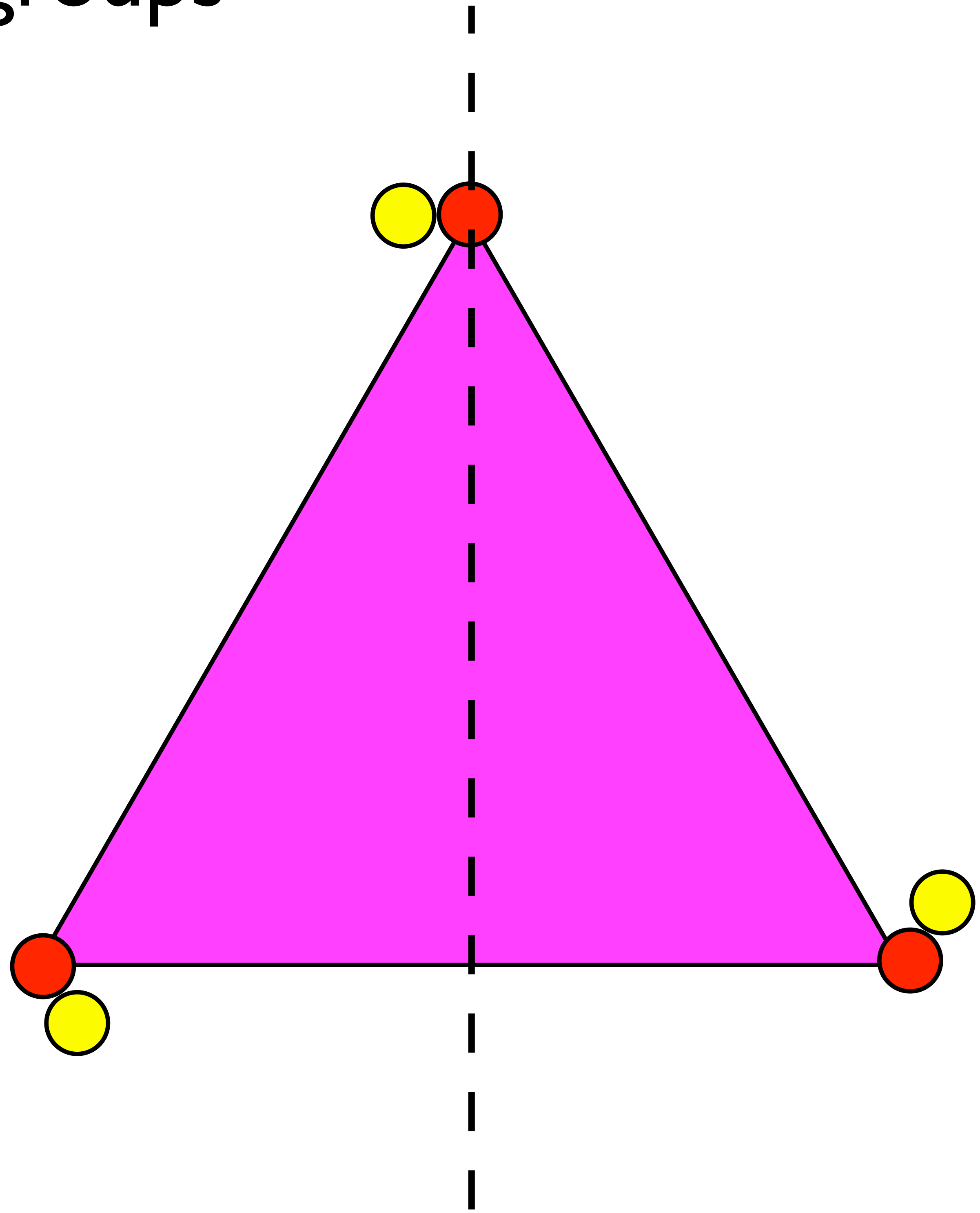
	E	D	F
E	E	D	F
D	D	F	E
F	F	E	D

Subgroups



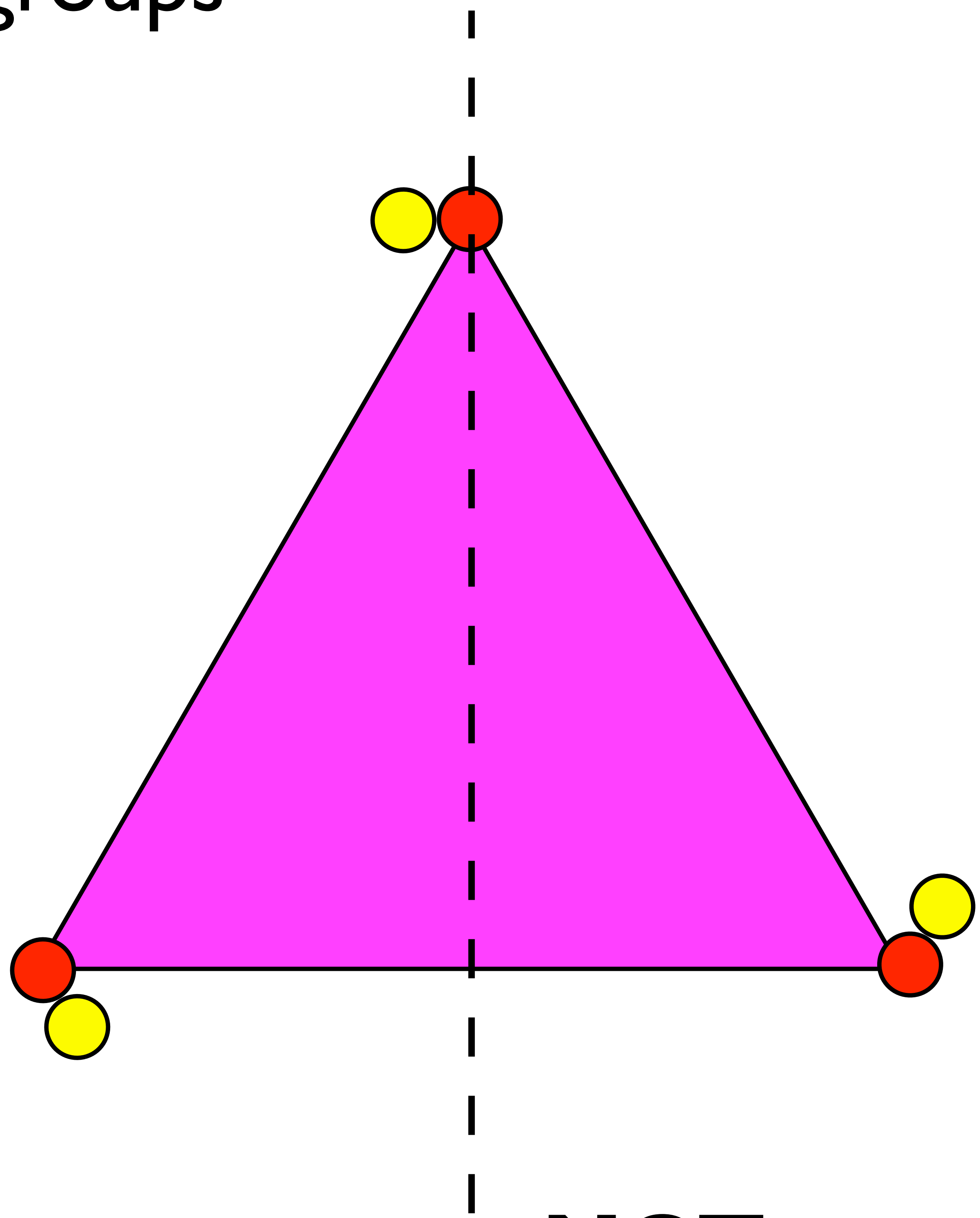
	E	D	F
E	E	D	F
D	D	F	E
F	F	E	D

Subgroups



	E	D	F
E	E	D	F
D	D	F	E
F	F	E	D

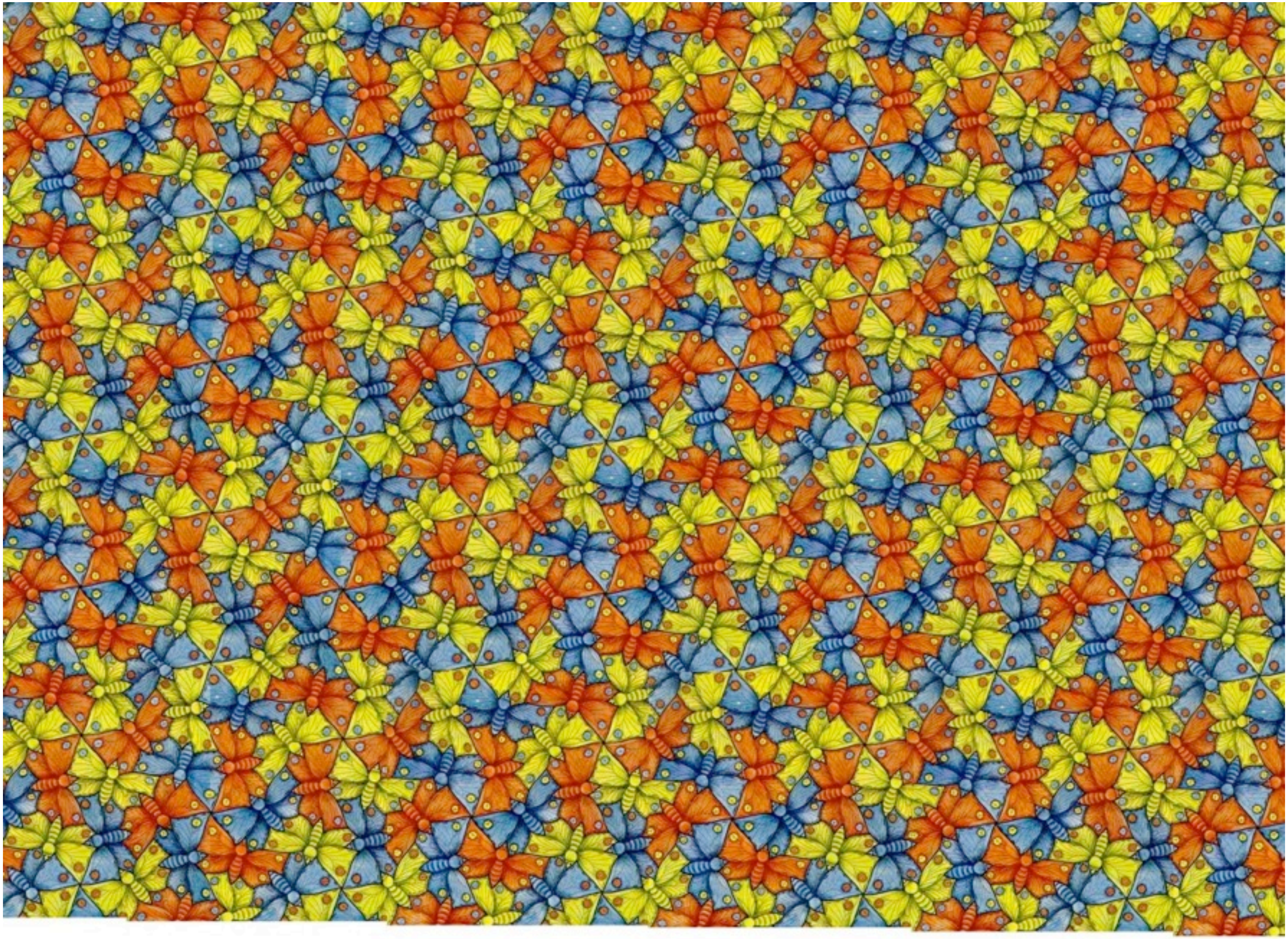
Subgroups



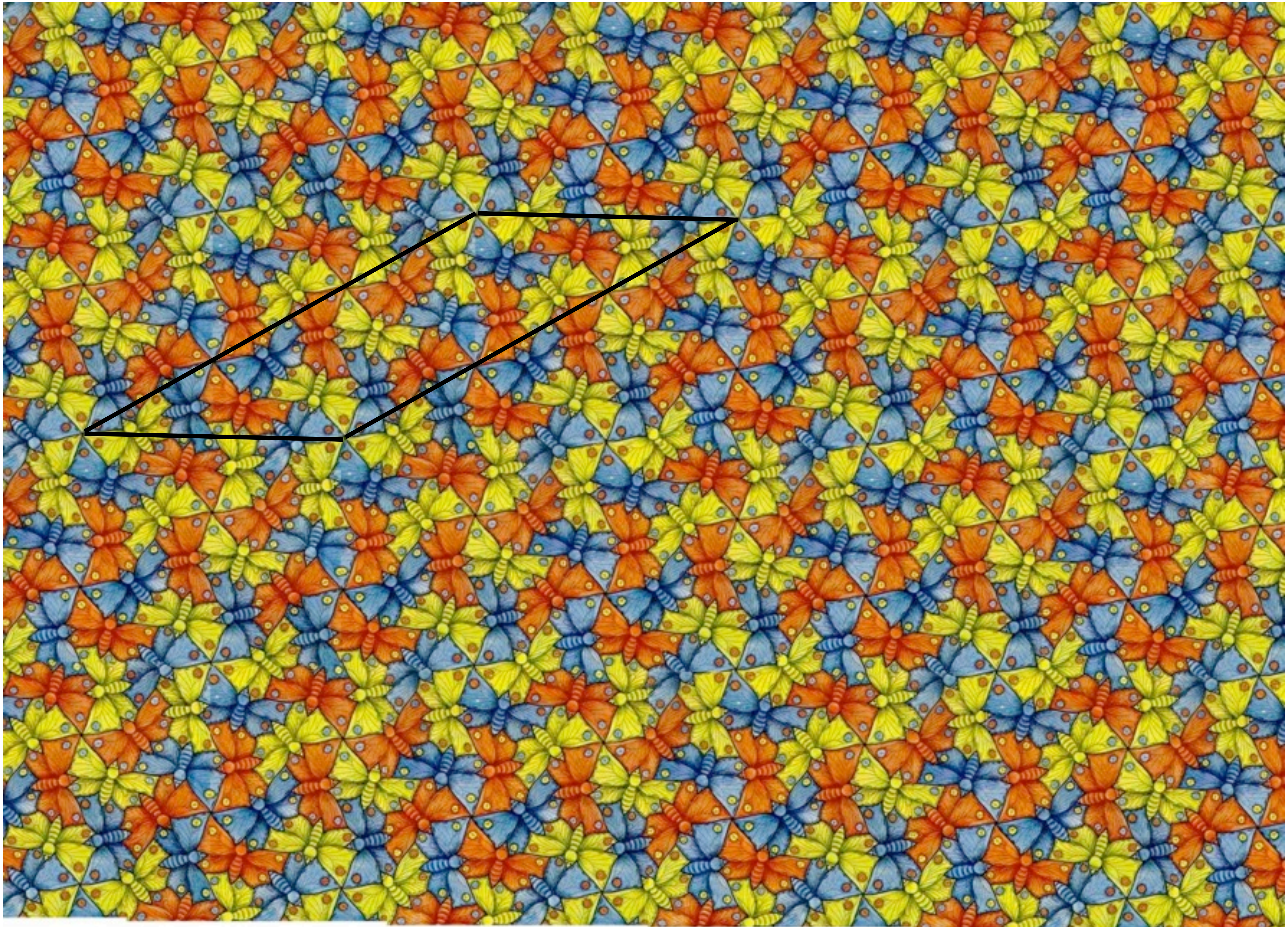
	E	D	F
E	E	D	F
D	D	F	E
F	F	E	D

NOT a symmetry axis anymore!

2 D crystal example



2 D crystal example



An element g_i of a group is said to be conjugate to another element g_j if a third x element exists so that:

$$g_j = x g_i x^{-1}$$

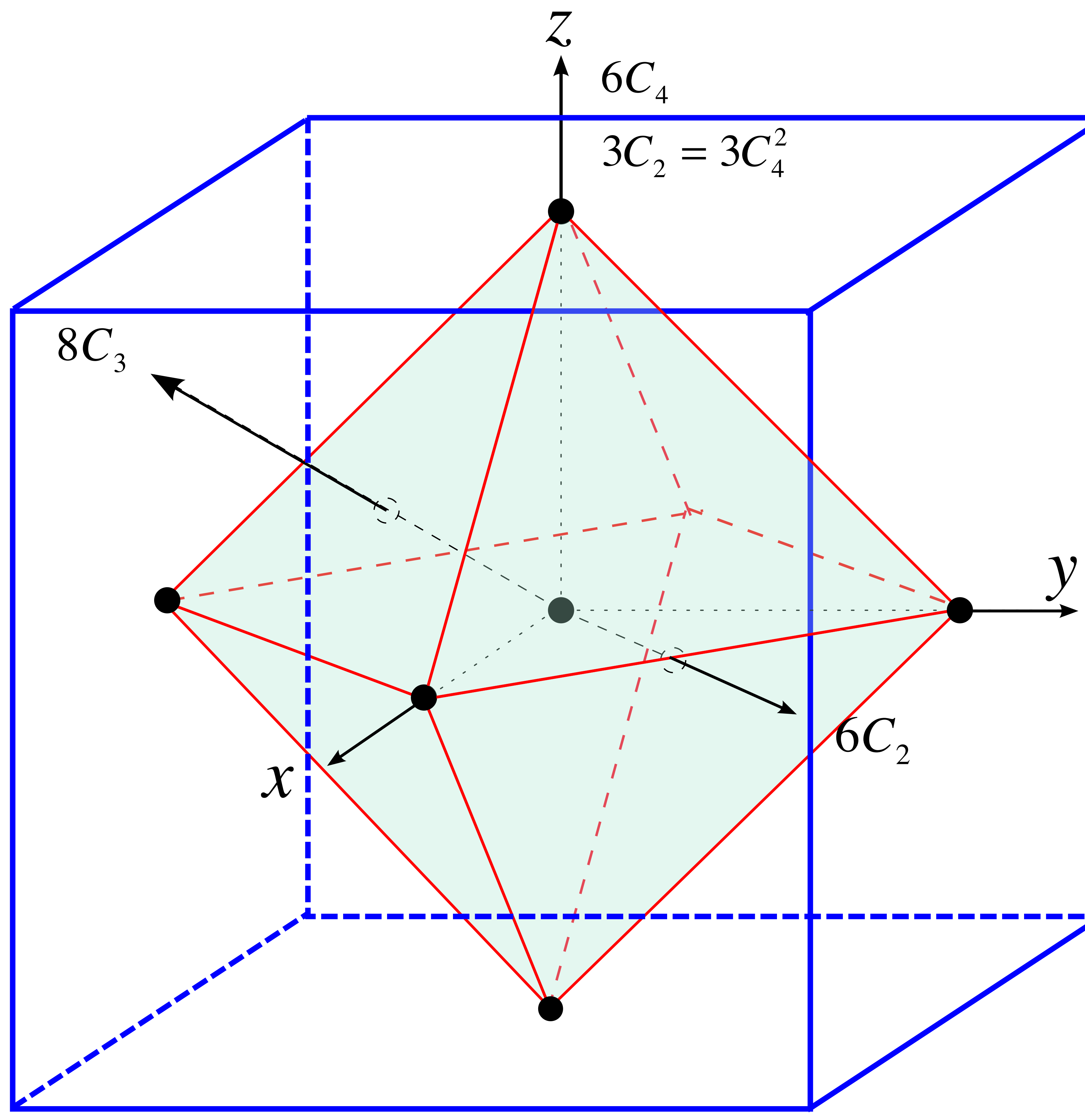
The set of conjugates is called class. Each element belongs to one class and one only and the identity element is a class by itself. C_{3v} consists of three classes:

$$C_1 = E;\ C_2 = A,B,C;\ C_3 = D,F$$

Point groups

Point Group	Essential Symmetry Elements
C_1	Identity only
C_s	One Symmetry plane
C_i	A centre of symmetry
C_n	One n-fold axis of symmetry
D_n	One C_n axis plus n C_2 axis perpendicular to it
C_{nv}	One C_n axis plus n vertical planes σ_v
C_{nh}	One C_n axis plus a horizontal plane σ_h
D_{nh}	Those of D_n plus a horizontal plane σ_h
D_{nd}	Those of D_n n dihedral planes σ_d
S_n (n even)	One n-fold alternating axis of symmetry
T_d	Those of a regular tedrahedron
O_h	Those of a regular octahedron of cube
I_h	Those of a regular icosahedron
H_h	Those of a sphere

Symmetry operations in a cube (O_h group)



Symmetry operations of the cube (O_h group)

Class	Symmetry operation	Coordinate transformation	Class	Symmetry operation	Coordinate transformation
E	E	x y z	I	I	-x -y -z
C_4^2	δ_{2x}	-x -y z	IC_4^2	$I\delta_{2x}$	x y -z
	δ_{2y}	x -y -z		$I\delta_{2y}$	-x y z
	δ_{2z}	-x y -z		$I\delta_{2z}$	x -y z
C_4	δ^{-1}_{4z}	-y x z	IC_4	$I\delta^{-1}_{4z}$	y -x -z
	δ_{4z}	y -x z		$I\delta_{4z}$	-y x -z
	δ^{-1}_{4x}	x -z y		$I\delta^{-1}_{4x}$	-x z -y
	δ_{4x}	x z -y		$I\delta_{4x}$	-x -z y
	δ^{-1}_{4y}	z y -x		$I\delta^{-1}_{4y}$	-z -y x
	δ_{4y}	-z y x		$I\delta_{4y}$	z -y -x
C_2	δ_{2xy}	y x -z	IC_2	$I\delta_{2xy}$	-y -x z
	δ_{2xz}	z -y x		$I\delta_{2xz}$	-z y -x
	δ_{2yz}	-x z y		$I\delta_{2yz}$	x -z -y
	δ_{2x-y}	-y -x -z		$I\delta_{2x-y}$	y x z
	δ_{2-xz}	-z -y -x		$I\delta_{2-xz}$	z y x
	δ_{2y-z}	-x -z -y		$I\delta_{2y-z}$	x z y
C_3	δ^{-1}_{3xyz}	z x y	IC_3	$I\delta^{-1}_{3xyz}$	-z -x -y
	δ_{3xyz}	y z x		$I\delta_{3xyz}$	-y -z -x
	δ^{-1}_{3x-yz}	z -x -y		$I\delta^{-1}_{3x-yz}$	-z x y
	δ_{3x-yz}	-y -z x		$I\delta_{3x-yz}$	y z -x
	δ^{-1}_{3x-y-z}	-z -x y		$I\delta^{-1}_{3x-y-z}$	z x -y
	δ_{3x-y-z}	-y z -x		$I\delta_{3x-y-z}$	y -z x
	δ^{-1}_{3xy-z}	-z x -y		$I\delta^{-1}_{3xy-z}$	z -x y
	δ_{3xy-z}	y -z -x		$I\delta_{3xy-z}$	-y z x

Representations

A representation is a collection of square non singular matrices associated with the elements of the group and which obey the group multiplication table

Representations

A representation is a collection of square non singular matrices associated with the elements of the group and which obey the group multiplication table

For the group C_{3v}

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

Representations of the group C_{3v}

the totally symmetric (unit) representation

$$\Gamma^{(1)}(E) = \Gamma^{(1)}(A) = \Gamma^{(1)}(B) = \Gamma^{(1)}(C) = \Gamma^{(1)}(D) = \Gamma^{(1)}(F) = 1$$

another 1d representation:

$$\Gamma^{(2)}(E) = 1$$

$$\Gamma^{(2)}(A) = \Gamma^{(2)}(B) = \Gamma^{(2)}(C) = -1$$

$$\Gamma^{(2)}(D) = \Gamma^{(2)}(F) = 1$$

Representations of the group C_{3v}

a 2 d representation

$$\Gamma^{(3)}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \Gamma^{(3)}(A) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\Gamma^{(3)}(B) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \qquad \Gamma^{(3)}(C) = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$\Gamma^{(3)}(D) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \qquad \Gamma^{(3)}(F) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

Representations of the group C_{3v}

a 3d representation

$$\Gamma^{(4)}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \Gamma^{(4)}(A) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\Gamma^{(4)}(B) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \Gamma^{(4)}(C) = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\Gamma^{(4)}(D) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \Gamma^{(4)}(F) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Representations of the group C_{3v}

another 3d representation

$$\Gamma^{(5)}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \Gamma^{(5)}(A) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\Gamma^{(5)}(B) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \Gamma^{(5)}(C) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

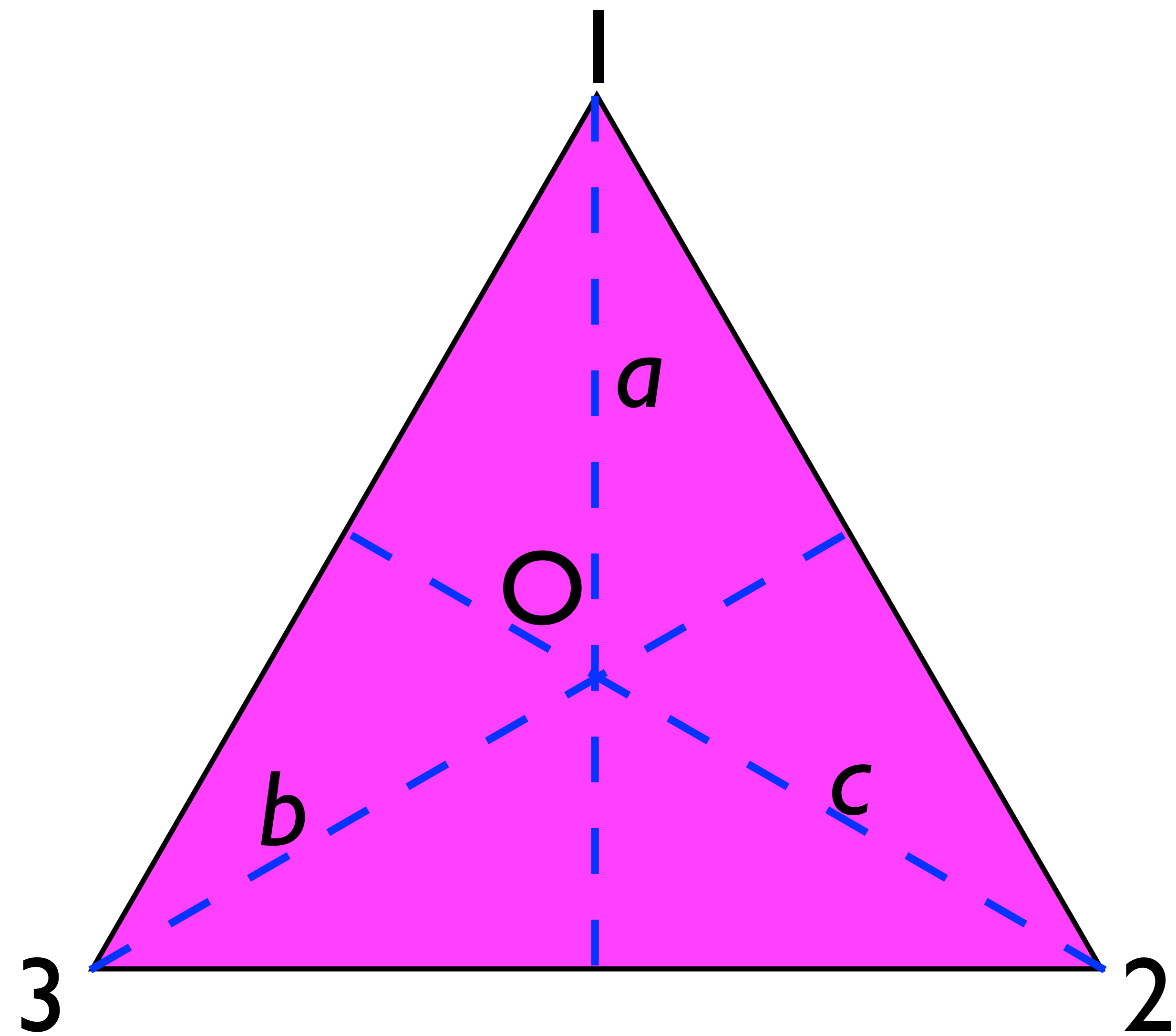
$$\Gamma^{(5)}(D) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \qquad \Gamma^{(5)}(F) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

Representations of the group C_{3v}

This 3d representation derives from the permutations of the vertexes associated with the symmetry operations.

σ_a (A) exchanges 2 with 3

C_3 (D) puts atom 2 in 1, 1 in 3 and 3 in 2...



$$\Gamma^{(5)}(A) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \qquad \Gamma^{(5)}(D) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

Representations of the group C_{3v}

a 6d representation

$$\Gamma^{(6)}(E)=\begin{pmatrix}1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&1&0&0&0\\0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\end{pmatrix}$$

$$\Gamma^{(6)}(A)=\begin{pmatrix}-1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&-1&0&0&0\\0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\end{pmatrix}$$

$$\Gamma^{(6)}(B)=\begin{pmatrix}\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0\\0&0&\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0\\0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\end{pmatrix}$$

$$\Gamma^{(6)}(C)=\begin{pmatrix}\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&0&0\\\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0\\0&0&\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0\\0&0&\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\end{pmatrix}$$

$$\Gamma^{(6)}(D)=\begin{pmatrix}-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0&0&0\\\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0\\0&0&-\frac{1}{2}&-\frac{\sqrt{3}}{2}&0&0\\0&0&\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\end{pmatrix}$$

$$\Gamma^{(6)}(F)=\begin{pmatrix}-\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0&0&0\\-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0&0&0\\0&0&-\frac{1}{2}&\frac{\sqrt{3}}{2}&0&0\\0&0&-\frac{\sqrt{3}}{2}&-\frac{1}{2}&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\end{pmatrix}$$

The $\Gamma^{(6)}$ matrices have a "block" form:

$$\Gamma^{(6)}(B) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

The $\Gamma^{(6)}$ matrices have a "block" form:

$$\Gamma^{(6)}(B) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

The $\Gamma^{(6)}$ matrices have a "block" form:

$$\Gamma^{(6)}(B)=\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

The $\Gamma^{(6)}$ matrices have a "block" form:

$$\Gamma^{(6)}(B) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

The $\Gamma^{(6)}$ matrices have a "block" form:

$$\Gamma^{(6)}(B) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

Reducible Representations

A representation is *reducible* if its matrices are in a block form:

$$\Gamma(R) = \begin{pmatrix} \Gamma^{(1)}(R) & 0 \\ 0 & \Gamma^{(2)}(R) \end{pmatrix}$$

the representation is said to be reducible into $\Gamma^{(1)}$ to $\Gamma^{(n)}$:

$$\Gamma = \Gamma^{(1)} \oplus \Gamma^{(2)}$$

The $\Gamma^{(6)}$ matrices have a "block" form:

$$\Gamma^{(6)}(B) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

The $\Gamma^{(6)}$ matrices have a "block" form:

$$\Gamma^{(6)}(B) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

where each block is a matrix of the $\Gamma^{(3)}$ and $\Gamma^{(1)}$ representations. We can write:

The $\Gamma^{(6)}$ matrices have a "block" form:

$$\Gamma^{(6)}(B)=\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

where each block is a matrix of the $\Gamma^{(3)}$ and $\Gamma^{(1)}$ representations. We can write:

$$\Gamma^{(6)}(B)=2\Gamma^{(3)}(B)\oplus 2\Gamma^{(1)}(B)$$

Representations of the group C_{3v}

The $\Gamma^{(6)}$ matrices have a "block" form:

$$\Gamma^{(6)}(B) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

where each block is a matrix of the $\Gamma^{(3)}$ and $\Gamma^{(1)}$ representations. We can write:

$$\Gamma^{(6)}(B) = 2\Gamma^{(3)}(B) \oplus 2\Gamma^{(1)}(B)$$

And in general:

The $\Gamma^{(6)}$ matrices have a "block" form:

$$\Gamma^{(6)}(B) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

where each block is a matrix of the $\Gamma^{(3)}$ and $\Gamma^{(1)}$ representations. We can write:

$$\Gamma^{(6)}(B) = 2\Gamma^{(3)}(B) \oplus 2\Gamma^{(1)}(B)$$

And in general: $$\boxed{\Gamma^{(6)} = 2\Gamma^{(3)} \oplus 2\Gamma^{(1)}}$$

Representations

Two representations connected by a *similarity* transformation:

$$\Gamma^{(j)} = S^{-1}\Gamma^{(i)}S$$

in which *S* is a non-singular matrix, are **equivalent**

For *finite* groups, any representation is equivalent to a *unitary* representation (i.e. composed of matrices for which:

$$\left|\det\left(\Gamma\left(R\right)\right) = 1\right|$$

Representations

For example the $\Gamma^{(5)}$ representation of the group C_{3v}:

$$\Gamma^{(5)}(E)=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\qquad \Gamma^{(5)}(A)=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}$$

$$\Gamma^{(5)}(B)=\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}\qquad \Gamma^{(5)}(C)=\begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix}$$

$$\Gamma^{(5)}(D)=\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}\qquad \Gamma^{(5)}(F)=\begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}$$

Is equivalent to a representation in block form which can be obtained by a similarity transformation with the matrix

$$S=\begin{pmatrix}0&\sqrt{\frac{2}{3}}&-\sqrt{\frac{1}{3}}\\-\sqrt{\frac{1}{2}}&-\sqrt{\frac{1}{6}}&-\sqrt{\frac{1}{3}}\\\sqrt{\frac{1}{2}}&-\sqrt{\frac{1}{6}}&-\sqrt{\frac{1}{3}}\end{pmatrix}$$

Representations

$$\Gamma^{(5')}(C) = S^{-1}\Gamma^{(5)}(C)S =$$

$$= \begin{pmatrix} 0 & -\sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} \\ -\sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \\ -\sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{3}} \\ \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{3}} \end{pmatrix} =$$

Representations

$$\Gamma^{(5')}(C) = S^{-1}\Gamma^{(5)}(C)S =$$

$$= \begin{pmatrix} 0 & -\sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} \\ -\sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \\ -\sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{3}} \\ \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{3}} \end{pmatrix} =$$

$$= \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Representations

$$\Gamma^{(5')}(C) = S^{-1}\Gamma^{(5)}(C)S =$$

$$= \begin{pmatrix} 0 & -\sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} \\ -\sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \\ -\sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{3}} \\ \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{3}} \end{pmatrix} =$$

$$= \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Representations

$$\Gamma^{(5')}(C) = S^{-1}\Gamma^{(5)}(C)S =$$

$$= \begin{pmatrix} 0 & -\sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} \\ -\sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{3}} \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{3}} \\ -\sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{3}} \\ \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{3}} \end{pmatrix} =$$

$$= \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad = \Gamma^{(3)}(B) \oplus \Gamma^{(1)}(B)$$

Characters

The *character* of a representation matrix is its trace (sum of its diagonal elements):

$$\chi^{(j)}(R) = \sum_{\alpha} \Gamma^{(j)}_{\alpha\alpha}(R)$$

Characters

The *character* of a representation matrix is its trace (sum of its diagonal elements):

$$\chi^{(j)}(R) = \sum_{\alpha} \Gamma^{(j)}_{\alpha\alpha}(R)$$

The traces of matrices connected by a similarity transformation are equal. Therefore:

Characters

The *character* of a representation matrix is its trace (sum of its diagonal elements):

$$\chi^{(j)}(R) = \sum_{\alpha} \Gamma^{(j)}_{\alpha\alpha}(R)$$

The traces of matrices connected by a similarity transformation are equal. Therefore:

a) elements of a group belonging to same *class* have the same *character* in any representation

Characters

The *character* of a representation matrix is its trace (sum of its diagonal elements):

$$\chi^{(j)}(R) = \sum_{\alpha} \Gamma^{(j)}_{\alpha\alpha}(R)$$

The traces of matrices connected by a similarity transformation are equal. Therefore:

a) elements of a group belonging to same *class* have the same *character* in any representation
b) *equivalent representations* have the the same set of characters

Characters

From the definition:

$$\chi^{(j)}(R) = \sum_{\alpha} \Gamma^{(j)}_{\alpha\alpha}(R)$$

Characters

From the definition:

$$\chi^{(j)}(R) = \sum_{\alpha} \Gamma^{(j)}_{\alpha\alpha}(R)$$

and the invariance under similarity transformation it follows that if

$$\Gamma^{(c)} = \Gamma^{(a)} \oplus \Gamma^{(b)}$$

Characters

From the definition:

$$\chi^{(j)}(R) = \sum_{\alpha} \Gamma^{(j)}_{\alpha\alpha}(R)$$

and the invariance under similarity transformation it follows that if

$$\Gamma^{(c)} = \Gamma^{(a)} \oplus \Gamma^{(b)}$$

then

$$\chi^{(c)}(R) = \chi^{(a)}(R) + \chi^{(b)}(R)$$

Irreducible Representations

The number of inequivalent irreducible representations of a group is equal to the number of classes. Their dimensions are restricted by:

$$\sum_i l_i^2 = h$$

where h is the order of the group

Irreducible Representations

$$\sum_i l_i^2 = h$$

For the C_{3v} group, the order h of the group is 6 and there are 3 classes. There are therefore 3 irreducible representations

$$6 = \sum_i l_i^2 = 1^2 + 1^2 + 2^2$$

two of which are unidimensional and one is bidimensional

Irreducible Representations

Schur's Lemma: Any matrix which commute with all the matrices of an irreducible representation must be a constant matrix $c\delta_{ij}$

Irreducible Representations

Orthogonality theorem: The non equivalent irreducible, unitary representations satisfy:

$$\sum_R \left(\Gamma^{(i)}_{\mu\nu}(R)\right)^* \left(\Gamma^{(j)}_{\alpha\beta}(R)\right) = \frac{h}{l_i}\delta_{ij}\delta_{\mu\alpha}\delta_{\nu\beta}$$

Irreducible Representations

$$\sum_R \left(\Gamma^{(i)}_{\mu\nu}(R)\right)^* \left(\Gamma^{(j)}_{\alpha\beta}(R)\right) = \frac{h}{l_i}\delta_{ij}\delta_{\mu\alpha}\delta_{\nu\beta}$$

By applying the orthogonality theorem to the diagonal elements

$$\sum_R \left(\Gamma^{(i)}_{\mu\mu}(R)\right)^* \left(\Gamma^{(j)}_{\alpha\alpha}(R)\right) = \frac{h}{l_i}\delta_{ij}\delta_{\mu\alpha}$$

we sum over μ and α:

$$\sum_R \left(\sum_\mu \Gamma^{(i)}_{\mu\mu}(R)^*\right)\left(\sum_\alpha \Gamma^{(j)}_{\alpha\alpha}(R)\right) = \sum_R \chi^{(i)}(R)^* \chi^{(j)}(R)$$

$$= \sum_{\mu=1}^{l_i} \sum_{\alpha=1}^{l_j} \frac{h}{l_i}\delta_{ij}\delta_{\mu\alpha} = \frac{h}{l_i}\delta_{ij} \sum_{\mu=1}^{l_i} \sum_{\alpha=1}^{l_j} \delta_{\mu\alpha}$$

Irreducible Representations

So we get the orthogonality relation for the characters of irreducible representations:

$$\sum_R \chi^{(i)}(R)^* \chi^{(j)}(R) = h\delta_{ij}$$

which implies that the characters χ^{red} of a reducible representation Γ^{red}, can be expressed in the form

$$\chi^{red}(R) = \sum_j a_j \chi^{(j)}(R)$$

in which:

$$a_i = \frac{1}{h}\sum_R \chi^{(i)}(R)^* \chi(R)$$

Irreducible Representations

The orthogonality relation for the characters of irreducible representations allows us to calculate the *character tables*.

For C_{3v} we get:

	E	A	B	C	D	F	6, elements 3 classes
$\Gamma^{(1)}$	1	1	1	1	1	1	
$\Gamma^{(2)}$	1	-1	-1	-1	1	1	
$\Gamma^{(3)}$	2	0	0	0	-1	-1	

3 irreducible representations

Irreducible Representations

Decomposition of the $\Gamma^{(5)}$ representation of the group C_{3v} using the character properties.

$$\Gamma^{(5)}(E)=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\qquad \Gamma^{(5)}(A)=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}\qquad \Gamma^{(5)}(B)=\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$$

$$\Gamma^{(5)}(C)=\begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix}\qquad \Gamma^{(5)}(D)=\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}\qquad \Gamma^{(5)}(F)=\begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}$$

Irreducible Representations

Decomposition of the $\Gamma^{(5)}$ representation of the group C_{3v} using the character properties.

$$\Gamma^{(5)}(E)=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\quad \Gamma^{(5)}(A)=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}\quad \Gamma^{(5)}(B)=\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$$

$$\Gamma^{(5)}(C)=\begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix}\quad \Gamma^{(5)}(D)=\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}\quad \Gamma^{(5)}(F)=\begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}$$

The characters are: $\chi^{(5)}(E)=3,\ \chi^{(5)}(A)=\chi^{(5)}(B)=\chi^{(5)}(C)=1,\ \chi^{(5)}(D)=\chi^{(5)}(F)=0$

Irreducible Representations

Decomposition of the $\Gamma^{(5)}$ representation of the group C_{3v} using the character properties.

$$\Gamma^{(5)}(E)=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\quad \Gamma^{(5)}(A)=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}\quad \Gamma^{(5)}(B)=\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$$

$$\Gamma^{(5)}(C)=\begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix}\quad \Gamma^{(5)}(D)=\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}\quad \Gamma^{(5)}(F)=\begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}$$

The characters are: $\chi^{(5)}(E)=3,\ \chi^{(5)}(A)=\chi^{(5)}(B)=\chi^{(5)}(C)=1,\ \chi^{(5)}(D)=\chi^{(5)}(F)=0$

Therefore:

$$a_1=\frac{1}{6}(3\times1+1\times1+1\times1+1\times1+0\times1+0\times1)=1$$

$$a_2=\frac{1}{6}\left(3\times1+1\times(-1)+1\times(-1)+1\times(-1)+0\times1+0\times1\right)=0$$

$$a_3=\frac{1}{6}\left(3\times2+1\times0+1\times0+1\times0+0\times1+0\times1\right)=1$$

Irreducible Representations

Decomposition of the $\Gamma^{(5)}$ representation of the group C_{3v} using the character properties.

$$\Gamma^{(5)}(E)=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\quad \Gamma^{(5)}(A)=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}\quad \Gamma^{(5)}(B)=\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$$

$$\Gamma^{(5)}(C)=\begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix}\quad \Gamma^{(5)}(D)=\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}\quad \Gamma^{(5)}(F)=\begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}$$

The characters are: $\chi^{(5)}(E)=3,\ \chi^{(5)}(A)=\chi^{(5)}(B)=\chi^{(5)}(C)=1,\ \chi^{(5)}(D)=\chi^{(5)}(F)=0$

Therefore:

$$a_1=\frac{1}{6}(3\times1+1\times1+1\times1+1\times1+0\times1+0\times1)=1$$

$$a_2=\frac{1}{6}\big(3\times1+1\times(-1)+1\times(-1)+1\times(-1)+0\times1+0\times1\big)=0$$

$$a_3=\frac{1}{6}(3\times2+1\times0+1\times0+1\times0+0\times1+0\times1)=1$$

i.e.: $$\Gamma^{(5)}=\Gamma^{(1)}\oplus\Gamma^{(3)}$$

Basis Functions

We can define sets of linearly independent functions φ whose transformations under the symmetry operations of the group P_r are given by:

$$P_R \varphi_k^{(j)}(\vec{r}) = \sum_{\lambda=1}^{n} \varphi_\lambda^{(j)}(\vec{r}) \Gamma_{\lambda k}^{(j)}(R)$$

i.e. the transformation of the basis set of the representation Γ^j under the symmetry operation R is described by the matrix Γ^j (R).

The φ functions are said to constitute a set of *basis functions* for the group

Basis Functions

We constructed Γ^3 in the group C_{3v} by considering the coordinate transformation. Therefore the functions

$$\varphi_1^{(3)}(\vec{r}) = x$$

$$\varphi_2^{(3)}(\vec{r}) = y$$

form a basis for the Γ^3 representation of the group.

The function:

$$\varphi_1^{(1)}(\vec{r}) = z$$

remains unchanged under any operation of the group and therefore constitute a basis for the Γ^1 representation, as well as

$$\varphi_1^{(1)'}(\vec{r}) = z^2$$

and

$$\varphi_1^{(1)''}(\vec{r}) = x^2 + y^2$$

Basis Functions

By stopping to second order functions (*d* orbitals!) we get for C_{3v} we can write:

	E	$3\sigma_v$	$2C_3$		
$\Gamma^{(1)}$	1	1	1	z	$x^2+y^2;z^2$
$\Gamma^{(2)}$	1	-1	1	R_z	
$\Gamma^{(3)}$	2	0	-1	$(x,y);(R_x,R_y)$	$(x^2-y^2,xy);(xz.yz)$

Product Representations

The direct product of two matrices is defined as:

$$\mathbf{C} = \mathbf{A} \times \mathbf{B} = \begin{pmatrix} A_{11}\mathbf{B} & A_{12}\mathbf{B} & \ldots\ldots \\ A_{21}\mathbf{B} & A_{22}\mathbf{B} & \ldots\ldots \\ \ldots\ldots & \ldots\ldots & \ldots\ldots \end{pmatrix}$$

or

$$C_{ik,jl} = A_{ij} B_{kl}$$

The characters are related by:

$$\chi(A \times B) = \chi(A)\chi(B)$$

Product Representations

If $\Gamma^{(\mu)}$ and $\Gamma^{(\nu)}$ are two representations of a group, the matrices

$$\Gamma^{(\mu\times\nu)}(R) = \Gamma^{(\mu)}(R) \times \Gamma^{(\nu)}(R)$$

constitute a representation $\Gamma^{(\mu\times\nu)}$ called *product representation*

The number of times the irreducible representation $\Gamma^{(\alpha)}$ appears in the product representation is given by:

$$a_{\alpha\mu\nu} = \frac{1}{h}\sum_R \chi^{(\alpha)}(R)^* \chi^{(\mu)}(R)\chi^{(\nu)}(R)$$

and in particular for α=1:

$$a_{1\mu\nu} = \delta_{\mu\nu}$$

Matrix Elements

As a consequence of the orthogonality theorem we have that:

$$\sum_R \Gamma^{(j)}_{\alpha\beta}(R) = 0$$

for any representation other then the unit representation.

If $\psi^{(j)}_\mu(\vec{r})$ is a member of a basis set for $\Gamma^{(j)}$ we have

$$\int \psi^{(j)}_\mu(\vec{r})d\vec{r} = \int P_R \psi^{(j)}_\mu(\vec{r})d\vec{r} = \sum_\alpha \Gamma^{(j)}_{\alpha\mu}(R) \int \psi^{(j)}_\alpha(\vec{r})d\vec{r}$$

by summing over all elements of the group we get

$$\sum_R \int \psi^{(j)}_\mu(\vec{r})d\vec{r} = \sum_\alpha \sum_R \Gamma^{(j)}_{\alpha\mu}(R) \int \psi^{(j)}_\alpha(\vec{r})d\vec{r}$$

Matrix Elements

As a consequence of the orthogonality theorem we have that:

$$\sum_R \Gamma^{(j)}_{\alpha\beta}(R) = 0$$

for any representation <u>other then the unit representation.</u>

If $\psi^{(j)}_{\mu}(\vec{r})$ is a member of a basis set for $\Gamma^{(j)}$ we have

$$\int \psi^{(j)}_{\mu}(\vec{r})d\vec{r} = \int P_R \psi^{(j)}_{\mu}(\vec{r})d\vec{r} = \sum_{\alpha} \Gamma^{(j)}_{\alpha\mu}(R) \int \psi^{(j)}_{\alpha}(\vec{r})d\vec{r}$$

by summing over all elements of the group we get

$$\sum_R \int \psi^{(j)}_{\mu}(\vec{r})d\vec{r} = \sum_{\alpha} \sum_R \Gamma^{(j)}_{\alpha\mu}(R) \int \psi^{(j)}_{\alpha}(\vec{r})d\vec{r} = 0$$

Matrix Elements

So, if $\psi_\mu^{(j)}(\vec{r})$ is a member of a basis set for $\Gamma^{(j)}$ **and** $\Gamma^{(j)}$ is **not** the unit representation we have:

$$\int \psi_\mu^{(j)}(\vec{r})d\vec{r} = 0$$

For a symmetric system, the ψ, Q and φ functions in the matrix element

$$M = \left\langle \psi_\alpha^{(i)} \middle| Q_\beta^{(j)} \middle| \varphi_\gamma^{(k)} \right\rangle = \int \psi_\alpha^{(i)}(\vec{r})^* Q_\beta^{(j)}(\vec{r}) \varphi_\gamma^{(k)}(\vec{r})d\vec{r}$$

transform according to the irreducible representations $\Gamma^{(i)}$, $\Gamma^{(j)}$ and $\Gamma^{(k)}$ respectively. Therefore the integrand belong to the product representation:

$$\Gamma^{(i)*} \times \Gamma^{(j)} \times \Gamma^{(k)} = \sum_\mu a_\mu \Gamma^{(\mu)}$$

Matrix Elements

So, if $\psi_{\mu}^{(j)}(\vec{r})$ is a member of a basis set for $\Gamma^{(j)}$ **and** $\Gamma^{(j)}$ is **not** the unit representation we have:

$$\int \psi_{\mu}^{(j)}(\vec{r})d\vec{r} = 0$$

For a symmetric system, the ψ, Q and φ functions in the matrix element

$$M = \left\langle \psi_{\alpha}^{(i)} \middle| Q_{\beta}^{(j)} \middle| \varphi_{\gamma}^{(k)} \right\rangle = \int \psi_{\alpha}^{(i)}(\vec{r})^{*} Q_{\beta}^{(j)}(\vec{r}) \varphi_{\gamma}^{(k)}(\vec{r}) d\vec{r}$$

transform according to the irreducible representations $\Gamma^{(i)}$, $\Gamma^{(j)}$ and $\Gamma^{(k)}$ respectively. Therefore the integrand belong to the product representation:

$$\Gamma^{(i)*} \times \Gamma^{(j)} \times \Gamma^{(k)} = \sum_{\mu} a_{\mu} \Gamma^{(\mu)}$$

The matrix element is ≠0 only if the product representation of the integrand contains the unit representation

Matrix Elements
Optical Selection Rules

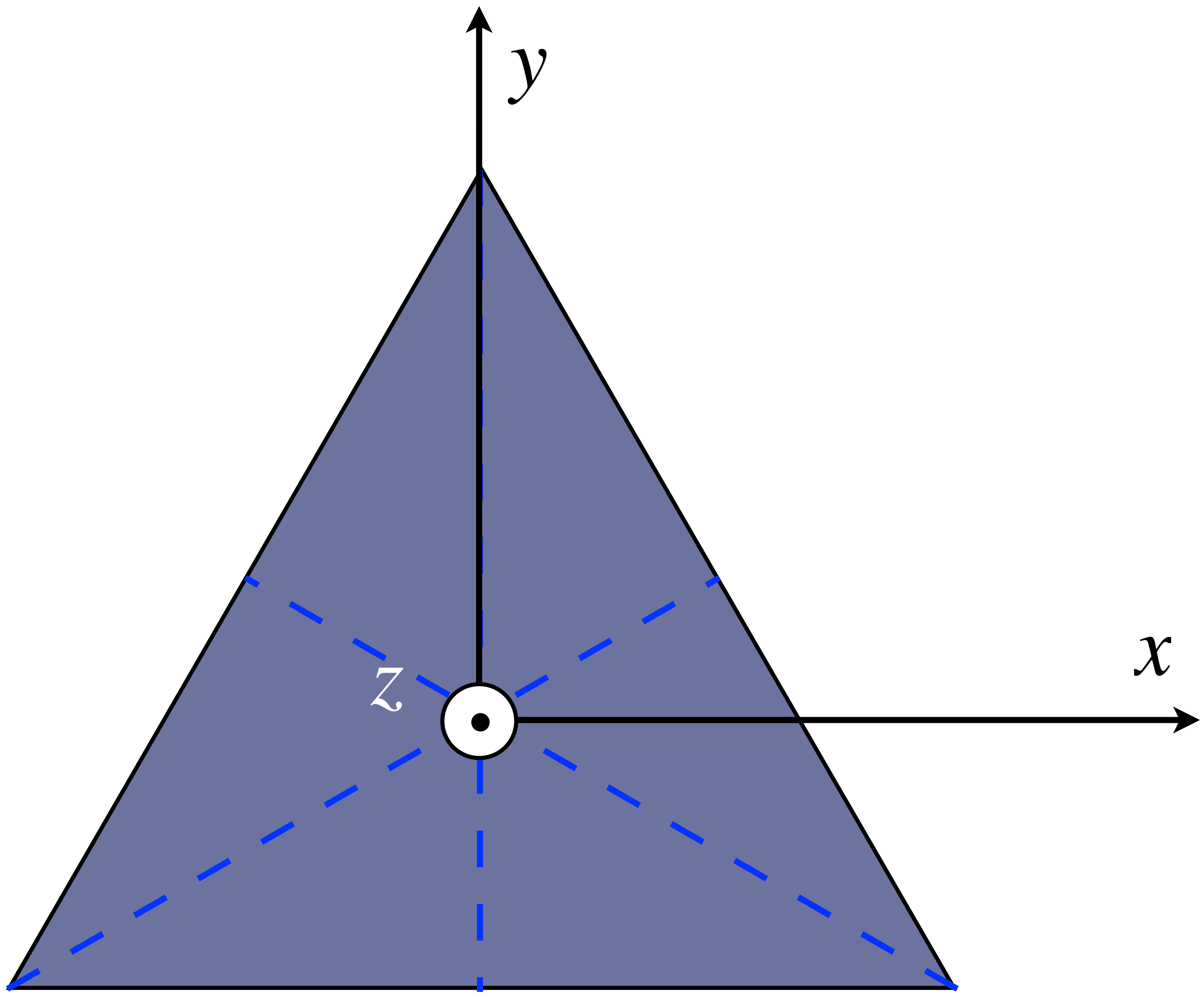
$$\mu(\hbar\omega) = \frac{4\pi^2 e^2}{nm^2 c\omega} \sum_{if} \left| \langle f | \hat{e} \cdot \vec{p} | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

Matrix Elements
Optical Selection Rules

$$\mu(\hbar\omega) = \frac{4\pi^2 e^2}{nm^2 c\omega} \sum_{if} \left| \langle f \left| \hat{e} \cdot \vec{p} \right| i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

this determines the symmetry of the em field

Matrix Elements
Optical Selection Rules



Matrix Elements
Optical Selection Rules

$$\mu(\hbar\omega) = \frac{4\pi^2 e^2}{nm^2 c\omega} \sum_{if} \left| \langle f | \hat{e} \cdot \vec{p} | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

C_{3v}	E	$3\sigma_v$	$2C_3$		
$\Gamma^{(1)}$	1	1	1	z	$x^2+y^2;z^2$
$\Gamma^{(2)}$	1	-1	1	R_z	
$\Gamma^{(3)}$	2	0	-1	$(x,y);(R_x,R_y)$	$(x^2-y^2,xy);(xz.yz)$

An em field polarized along z belongs to the $\Gamma^{(1)}$ representation

Optical Selection Rules

	E	*2C₃*	*3C₂*
$\Gamma^{(1)}$	1	1	1
$\Gamma^{(2)}$	1	1	-1
$\Gamma^{(3)}$	2	-1	0

	E	*2C₃*	*3C₂*	*Allowed?*
$\langle\Gamma^{(1)} \vert \Gamma^{(1)} \vert \Gamma^{(1)}\rangle$	1	1	1	YES
$\langle\Gamma^{(1)} \vert \Gamma^{(1)} \vert \Gamma^{(2)}\rangle$	1	1	-1	NO
$\langle\Gamma^{(2)} \vert \Gamma^{(1)} \vert \Gamma^{(2)}\rangle$	1	1	1	YES
$\langle\Gamma^{(1)} \vert \Gamma^{(1)} \vert \Gamma^{(3)}\rangle$	2	-1	0	NO
$\langle\Gamma^{(2)} \vert \Gamma^{(1)} \vert \Gamma^{(3)}\rangle$	2	-1	0	NO
$\langle\Gamma^{(3)} \vert \Gamma^{(1)} \vert \Gamma^{(3)}\rangle$	4	1	0	YES

An em field polarized along z belongs to the $\Gamma^{(1)}$ representation

Matrix Elements
Optical Selection Rules

C_{3v}	E	$3\sigma_v$	$2C_3$		
$\Gamma^{(1)}$	1	1	1	z	$x^2+y^2;z^2$
$\Gamma^{(2)}$	1	-1	1	R_z	
$\Gamma^{(3)}$	2	0	-1	$(x,y);(R_x,R_y)$	$(x^2-y^2,xy);(xz.yz)$

Note that e.m. field polarized in the xy plane would belong to the $\Gamma^{(3)}$ representation and, because of the C_3 symmetry the direction within the plane is **irrelevant**!

This is true for all cases in which there is a C_n symmetry axis obviously for n>2

Matrix Elements
Optical Selection Rules

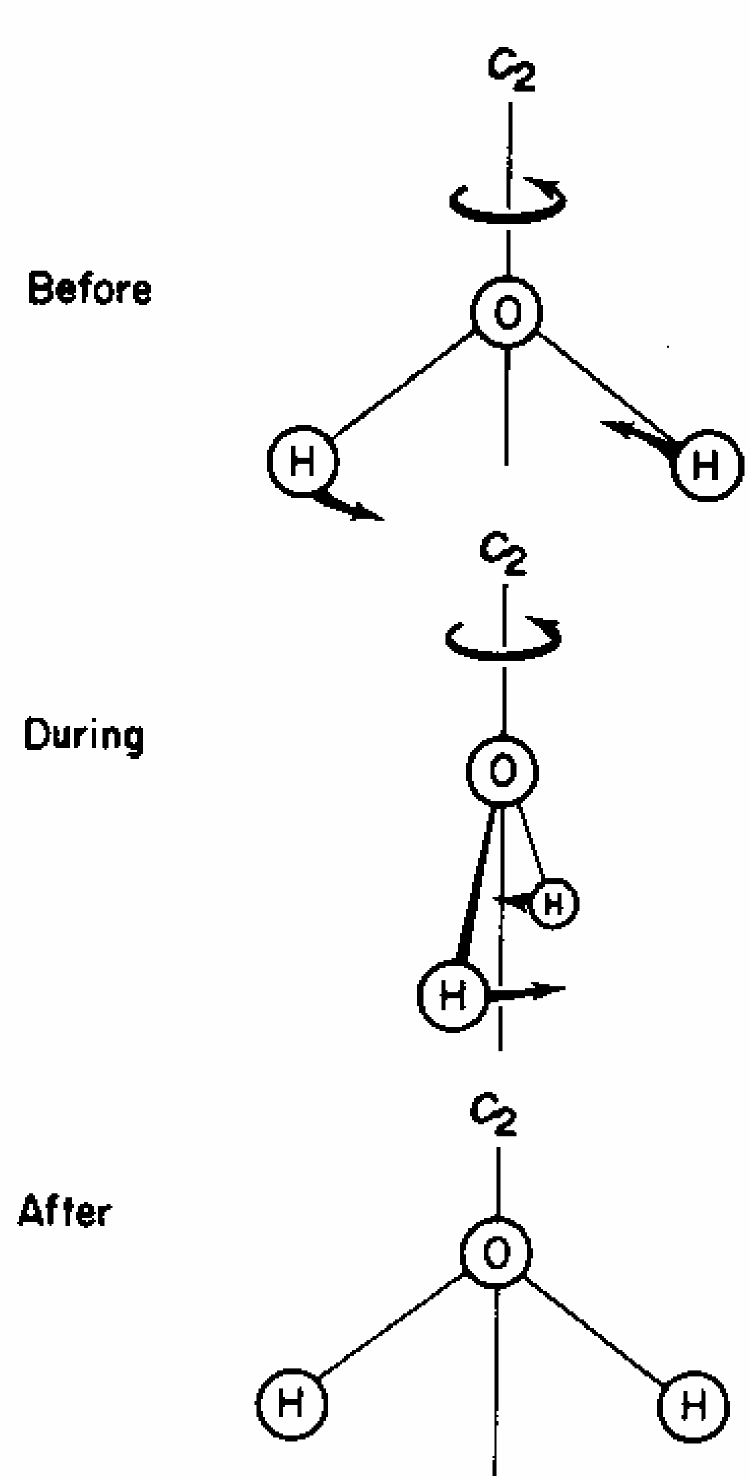
For the C_{2v} symmetry (e.g. the water molecule), the x, y and z directions are non equivalent

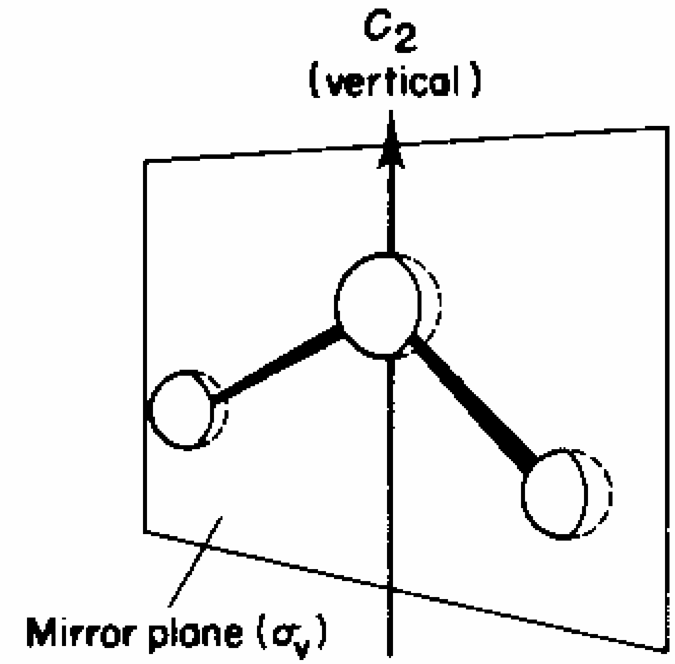
C_{2v}	E	$\sigma_v(xz)$	$\sigma_v(yz)$	C_2		
A_1	1	1	1	1	z	$x^2;y^2;z^2$
A_2	1	-1	-1	1	R_z	xy
B_1	1	1	-1	-1	$x;R_y$	xz
B_2	1	-1	1	-1	$y;R_x$	yz

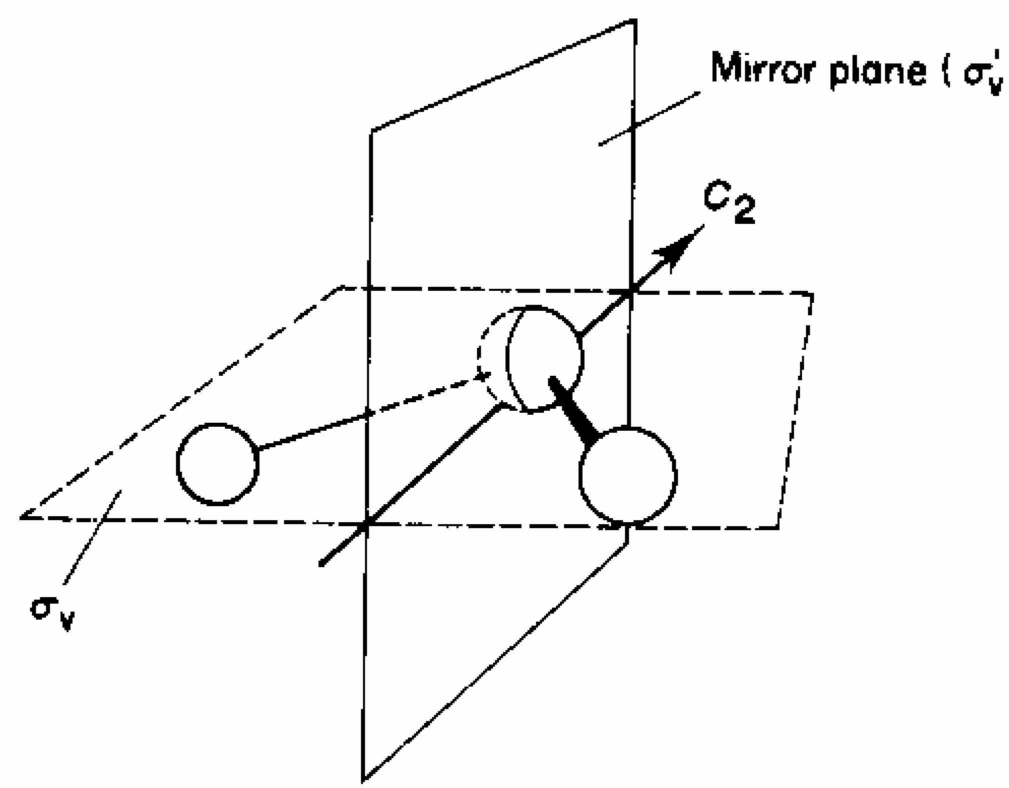
Water

- Consider how the following orbitals behave when subjected to the symmetry operations of the point group C_{2v}
  – O 2s, O $2p_x$ $2p_z$ and $2p_y$
  – H1s + H2s and H1s - H2s

Symmetry elements for H_2O







Transformation of H_{1s} orbitals in H_2O

- We can classify the combinations 1s(A) + 1s(B) and 1s(A) - 1s(B) by how they transform when the symmetry operations of the point group for the molecule (C_{2v}) are applied

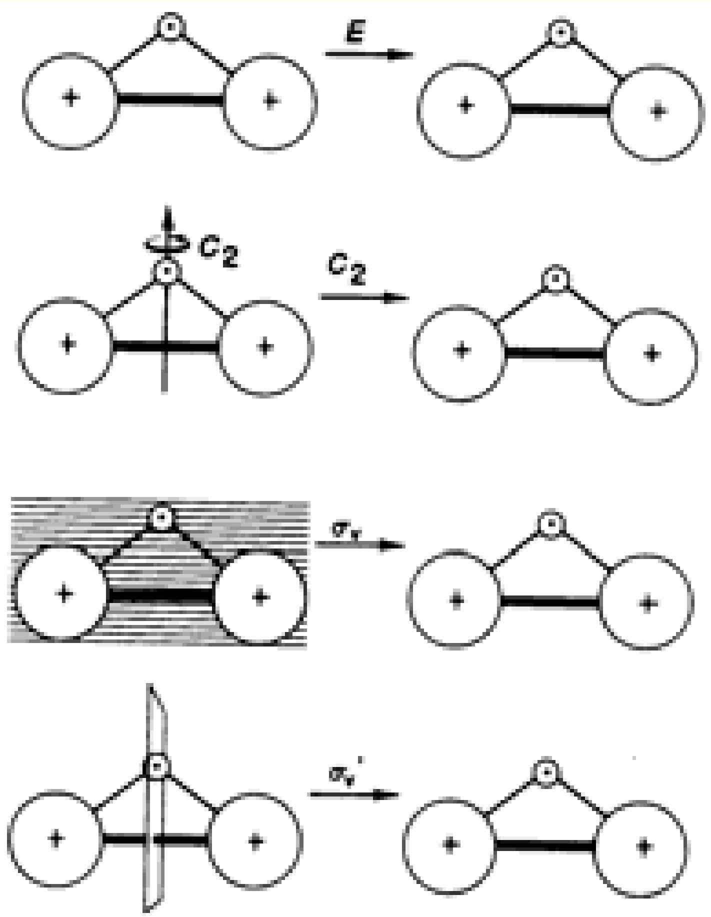


Figure 3.2 The transformations of the H–H bonding orbital of H_2 under the symmetry operations of the C_{2v} point group.

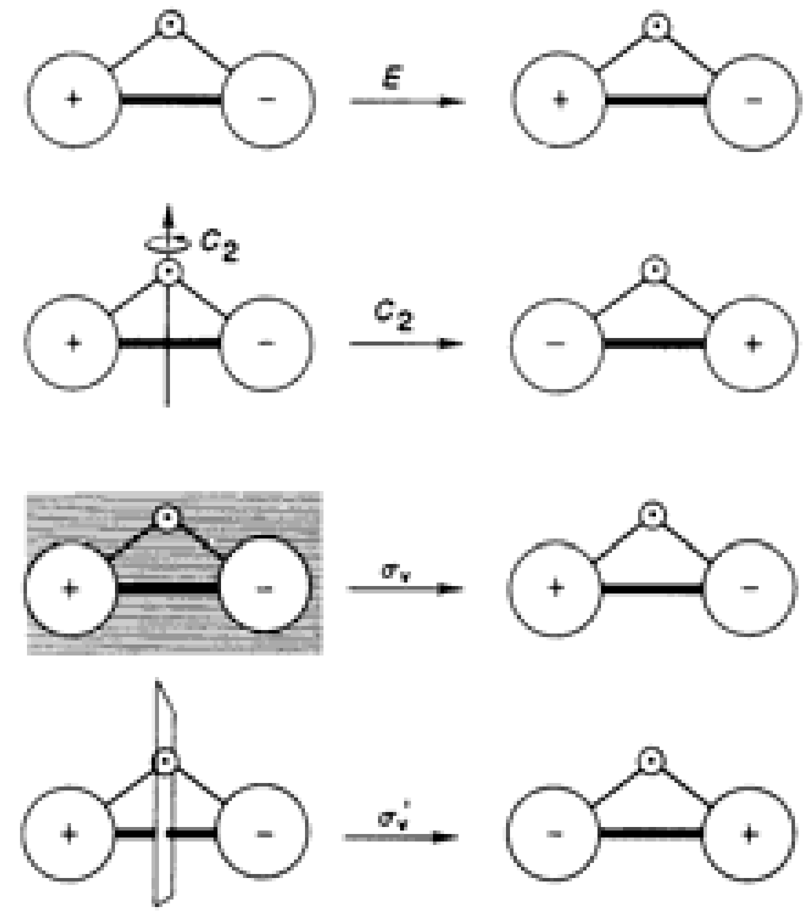


Figure 3.3 The transformations of the H–H antibonding orbital of H_2 under the symmetry operations of the C_{2v} point group. The point of interest is a comparison of the phases of this orbital 'before' (left) and 'after'.

Transformation of O_{pz} orbital in H_2O

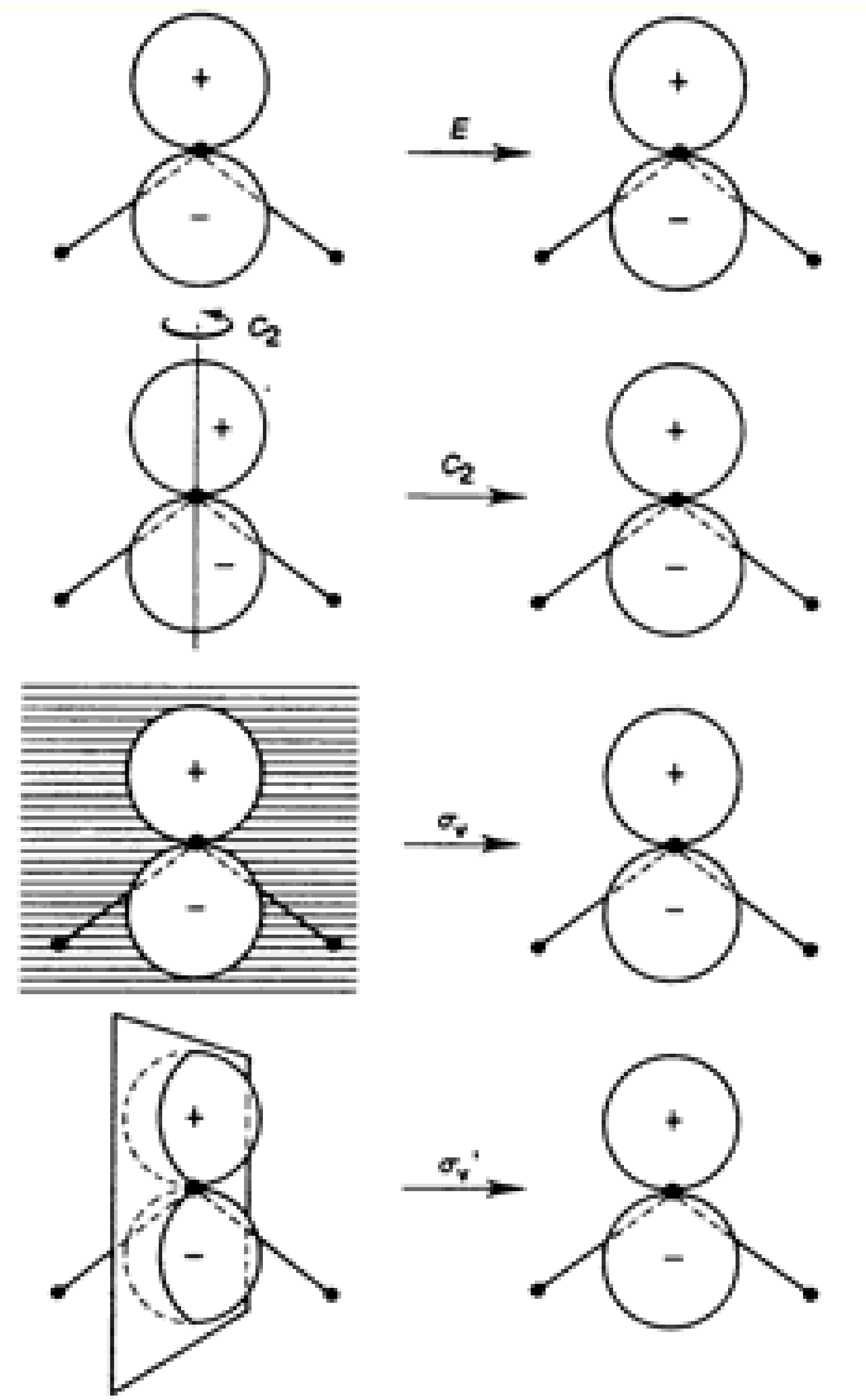


Figure 2.12 The effects of the symmetry operations of the C_{2v} point group on the oxygen $2p_z$ orbital in the water molecule. The point of importance is the relative phases of the orbital 'before' (left) and 'after' (right).

Transformation of the other O orbitals in H_2O

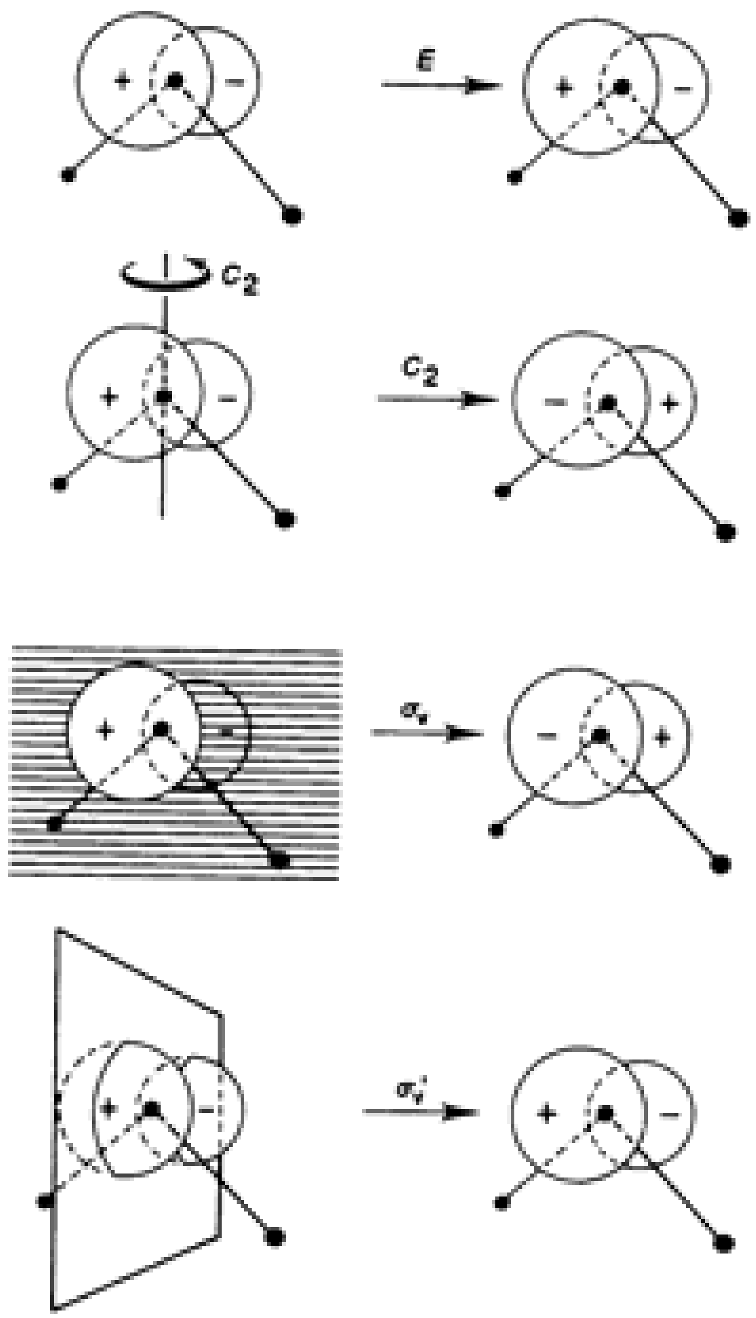


Figure 2.10 The effects of the symmetry operations of the C_{2v} point group on the oxygen $2p_x$ orbital in the water molecule. The point of importance is the relative phases of the orbital 'before' (left) and 'after' (right).

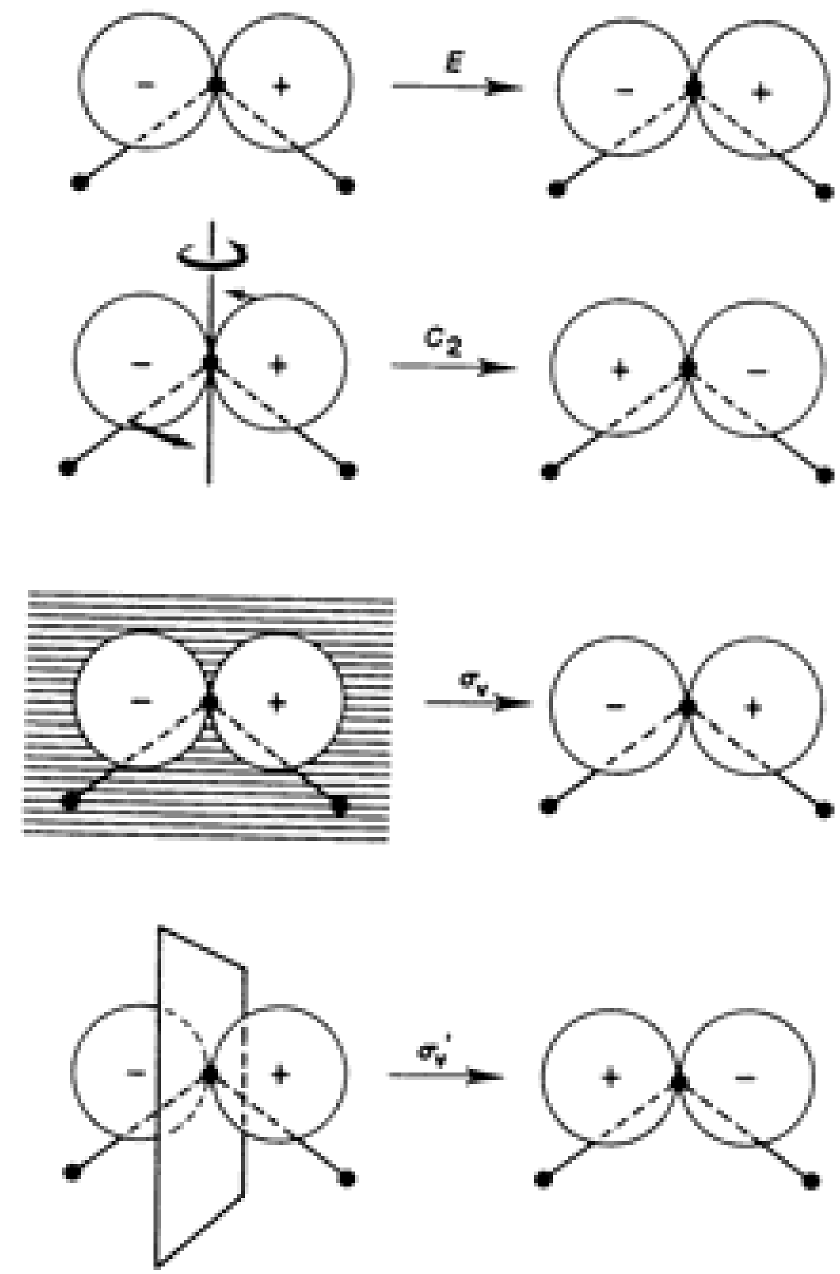


Figure 2.8 The effects of the symmetry operations of the C_{2v} point group on the oxygen $2p_y$ orbital in the water molecule. The point of importance is the relative phases of the orbital 'before' (left) and 'after' (right).

MO diagram for H_2O

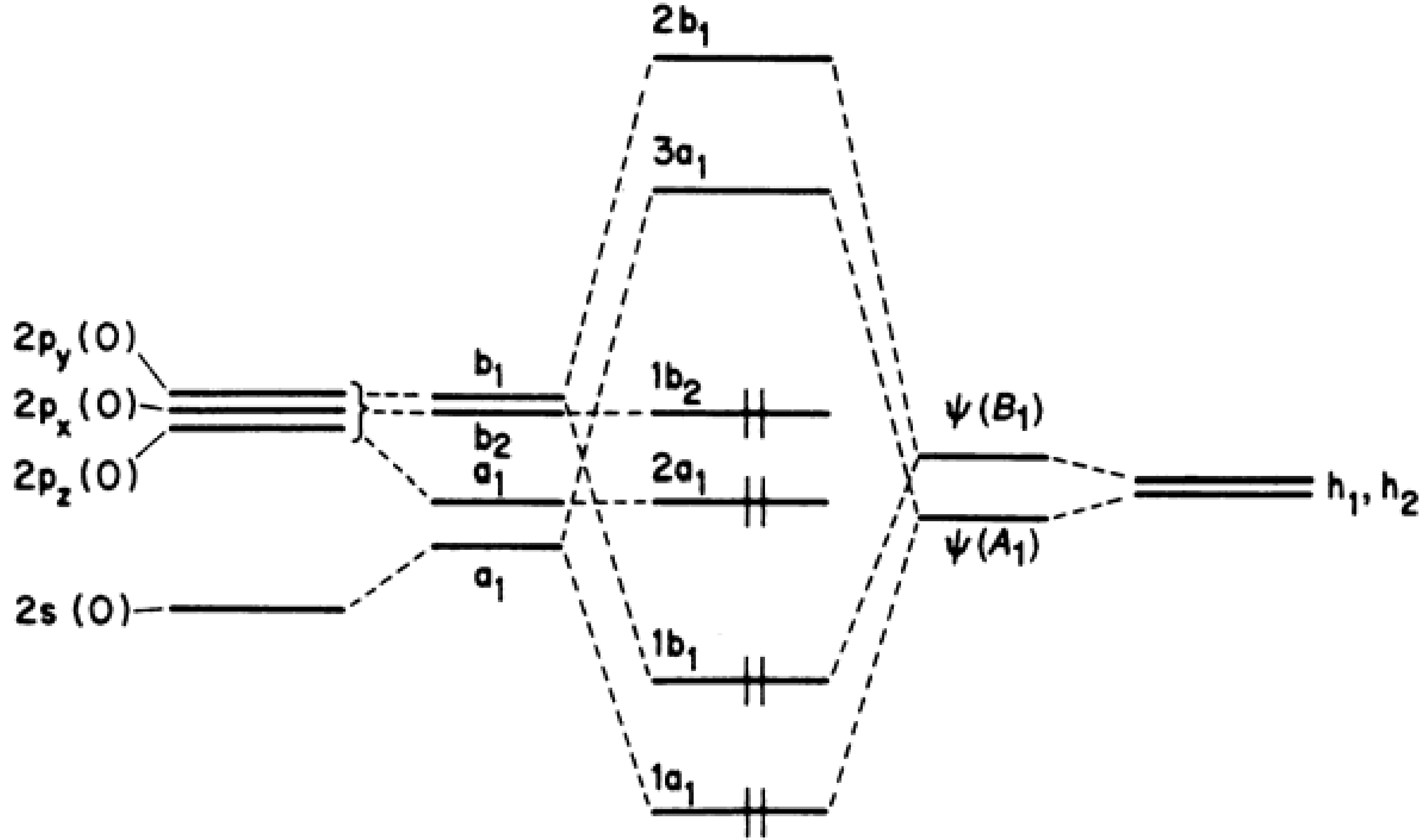
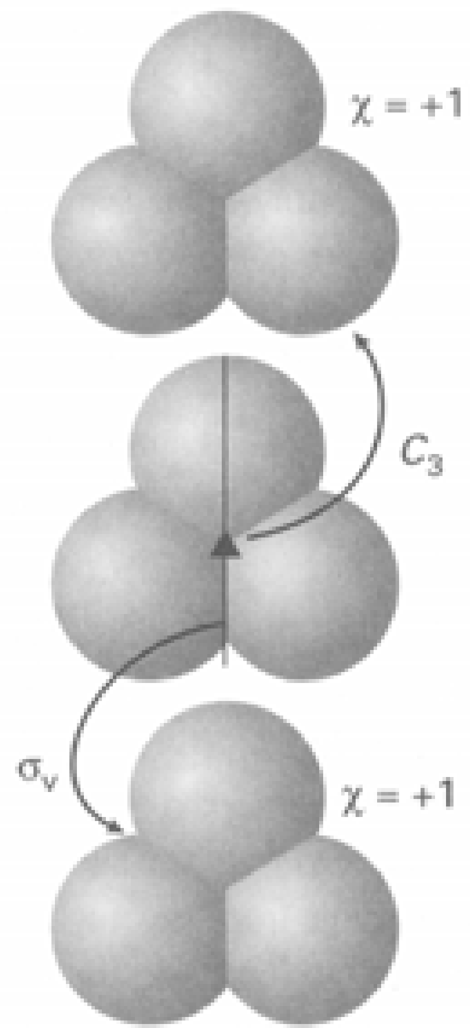


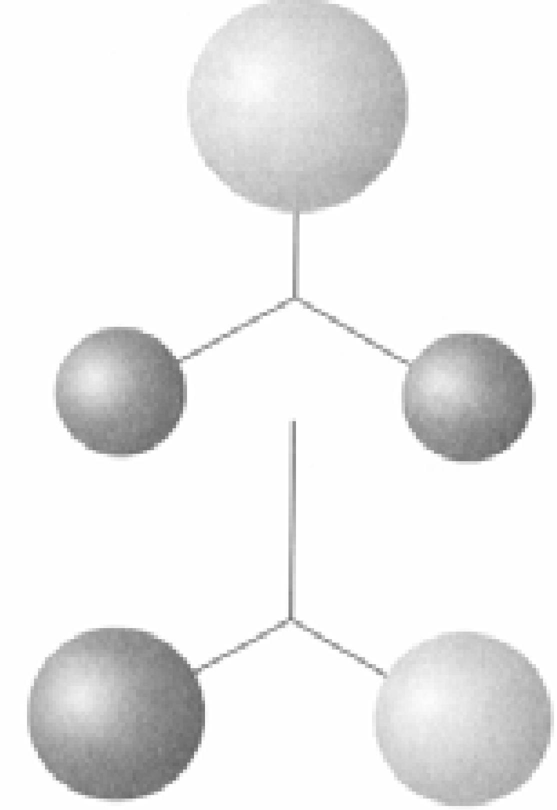
Figure 3.11 A schematic molecular orbital energy level diagram for H_2O.

SALCS for NH_3

Transforms as A_1



4.17 The combination $\phi_1 = \phi_A + \phi_B + \phi_C$ of the three H1*s* orbitals in the C_{3v} molecule NH_3 remains unchanged under a C_3 rotation and under any of the vertical reflections.

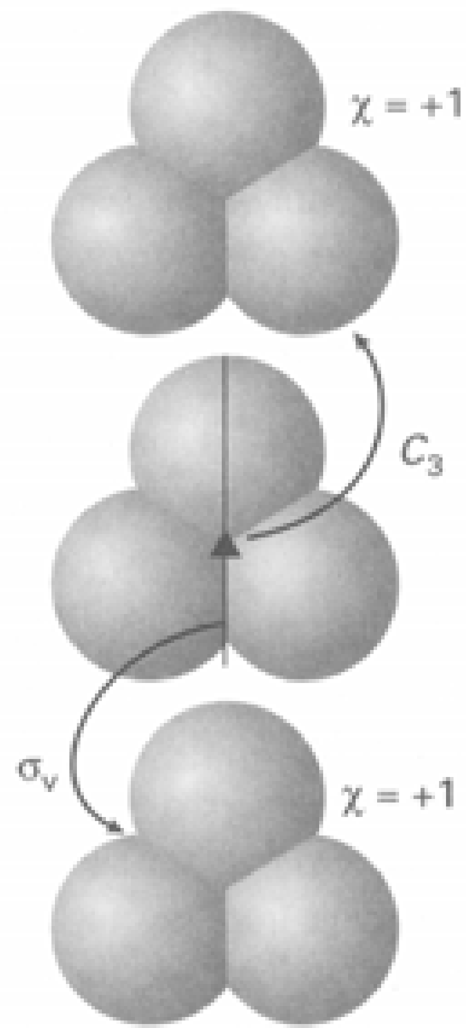


4.15 The combination of H1*s* orbitals that are used to form *e* orbitals in NH_3. They overlap the p_x and p_y orbitals on the N atom.

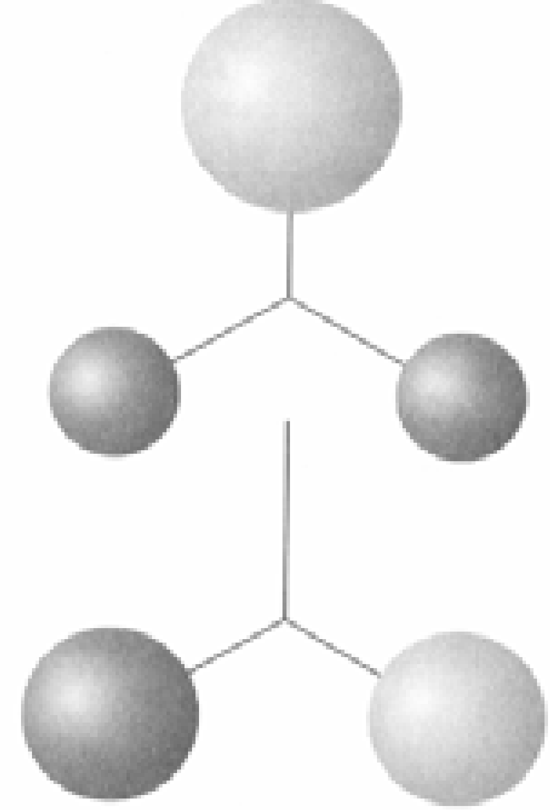
Transform as E

SALCS for NH_3

Transforms as A_1



4.17 The combination $\phi_1 = \phi_A + \phi_B + \phi_C$ of the three H1*s* orbitals in the C_{3v} molecule NH_3 remains unchanged under a C_3 rotation and under any of the vertical reflections.

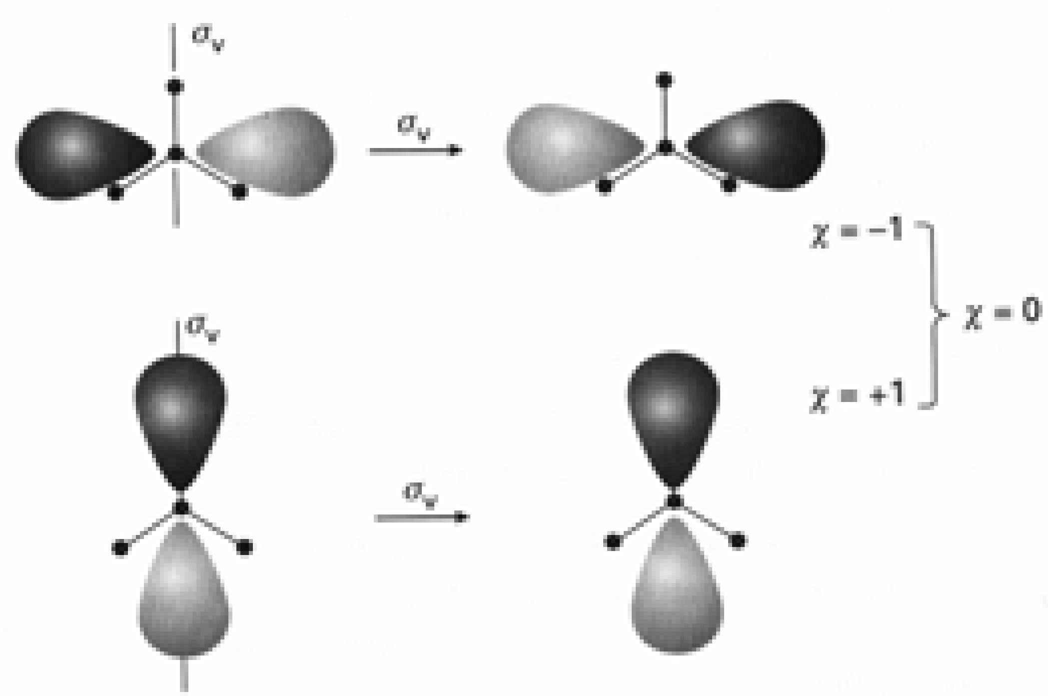


4.15 The combination of H1*s* orbitals that are used to form *e* orbitals in NH_3. They overlap the p_x and p_y orbitals on the N atom.

Transform as E

Symmetry of N orbitals in NH_3

- The N $2p_z$ orbital and the N 2s orbital transform as A_1 in the point group C_{3v}
- N $2p_x$ and $2p_y$ transform as E



4.20 An N2p_x orbital in NH_3 changes sign under a σ_v reflection but an N2p_y orbital is left unchanged. Hence the degenerate pair jointly has character 0 for this operation. The plane of the paper is the xy-plane.

C_{3v} (3m)	E	$2C_3$	$3\sigma_v$		$h = 6$
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, xy)(xz, yz)$

Examples of vibrational selection rules

C_{2v} (2mm)	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		$h = 4$
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

A_1, B_1 and B_2 symmetry vibrations will be IR active.

A_1, A_2, B_1 and B_2 symmetry vibrations will be Raman active.

C_{3v} (3m)	E	$2C_3$	$3\sigma_v$		$h = 6$
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

A_1 and E symmetry vibrations will be IR active.

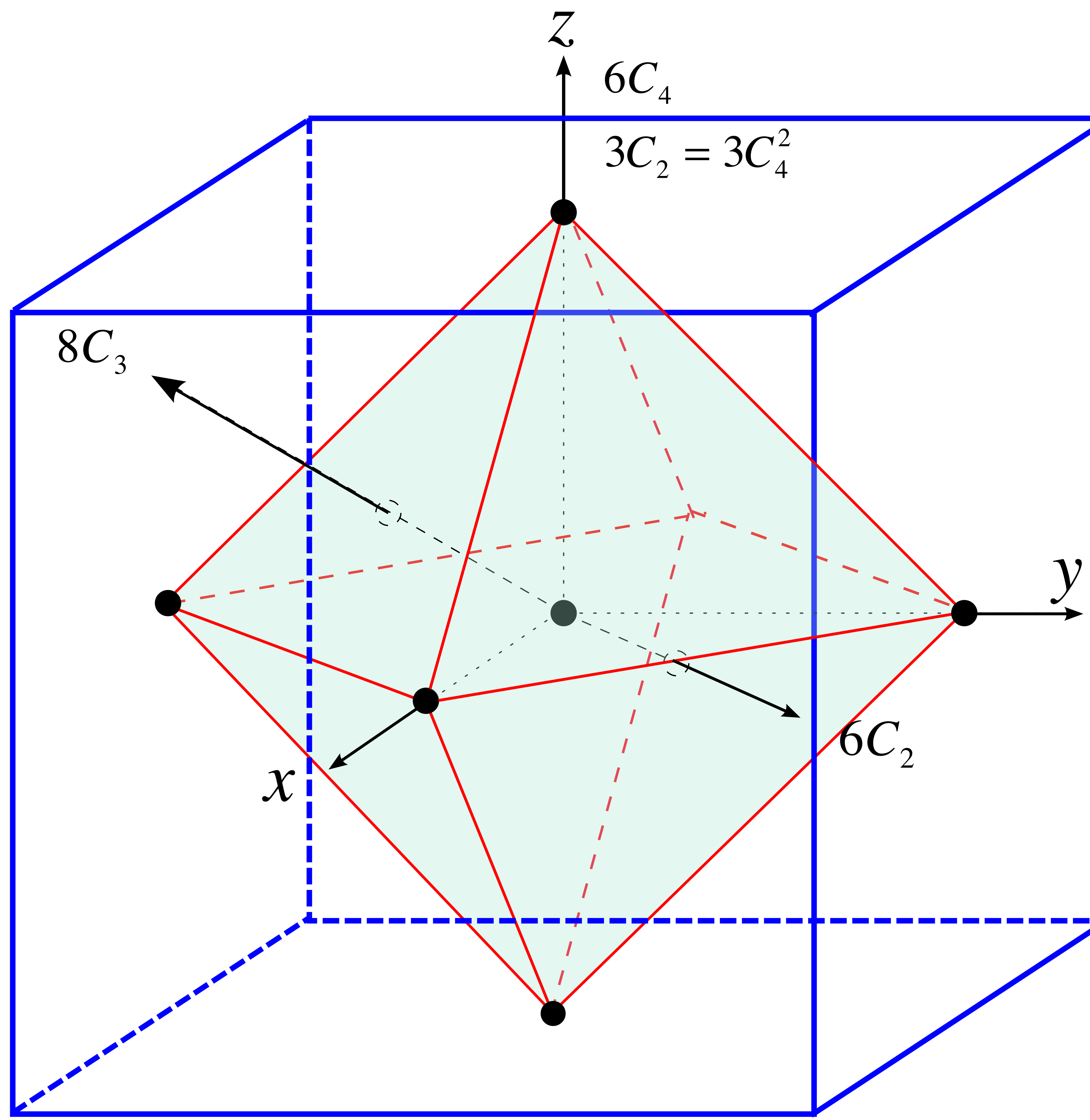
A_1, and E symmetry vibrations will be Raman active.

C_{4v} (4mm)	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		$h = 8$
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

A_1, and E symmetry vibrations will be IR active.

A_1, B_1, B_2 and E symmetry vibrations will be Raman active.

Symmetry operations in a cube (O_h group)



Optical Selection Rules

Character Table and Bases for the Cubic Group O_h

Repr.	Basis	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	i	$3iC_4^2$	$6iC_4$	$6iC_2$	$8iC_3$
Γ_1	1	1	1	1	1	1	1	1	1	1	1
Γ_2	$x^4(y^2-z^2)+$ $y^4(z^2-x^2)+$ $z^4(x^2-y^2)$	1	1	-1	-1	1	1	1	-1	-1	1
Γ_{12}	x^2-y^2 $2z^2-x^2-y^2$	2	2	0	0	-1	2	2	0	0	-1
Γ'_{15}	$xy(x^2-y^2)$ $yz(y^2-z^2)$ $zx(z^2-x^2)$	3	-1	1	-1	0	3	-1	1	-1	0
Γ'_{25}	xy, yz, zx	3	-1	-1	1	0	3	-1	-1	1	0
Γ'_1	$xyz[x^4(y^2-z^2)+$ $y^4(z^2-x^2)+$ $z^4(x^2-y^2)]$	1	1	1	1	1	-1	-1	-1	-1	-1
Γ'_2	xyz	1	1	-1	-1	1	-1	-1	1	1	-1
Γ'_{12}	$xyz(x^2-y^2)$ $xyz(2z^2-x^2-y^2)$	2	2	0	0	-1	-2	-2	0	0	1
Γ_{15}	x, y, z	3	-1	1	-1	0	-3	1	-1	1	0
Γ_{25}	$z(x^2-y^2)$ $x(y^2-z^2)$ $y(z^2-x^2)$	3	-1	-1	1	0	-3	1	1	-1	0

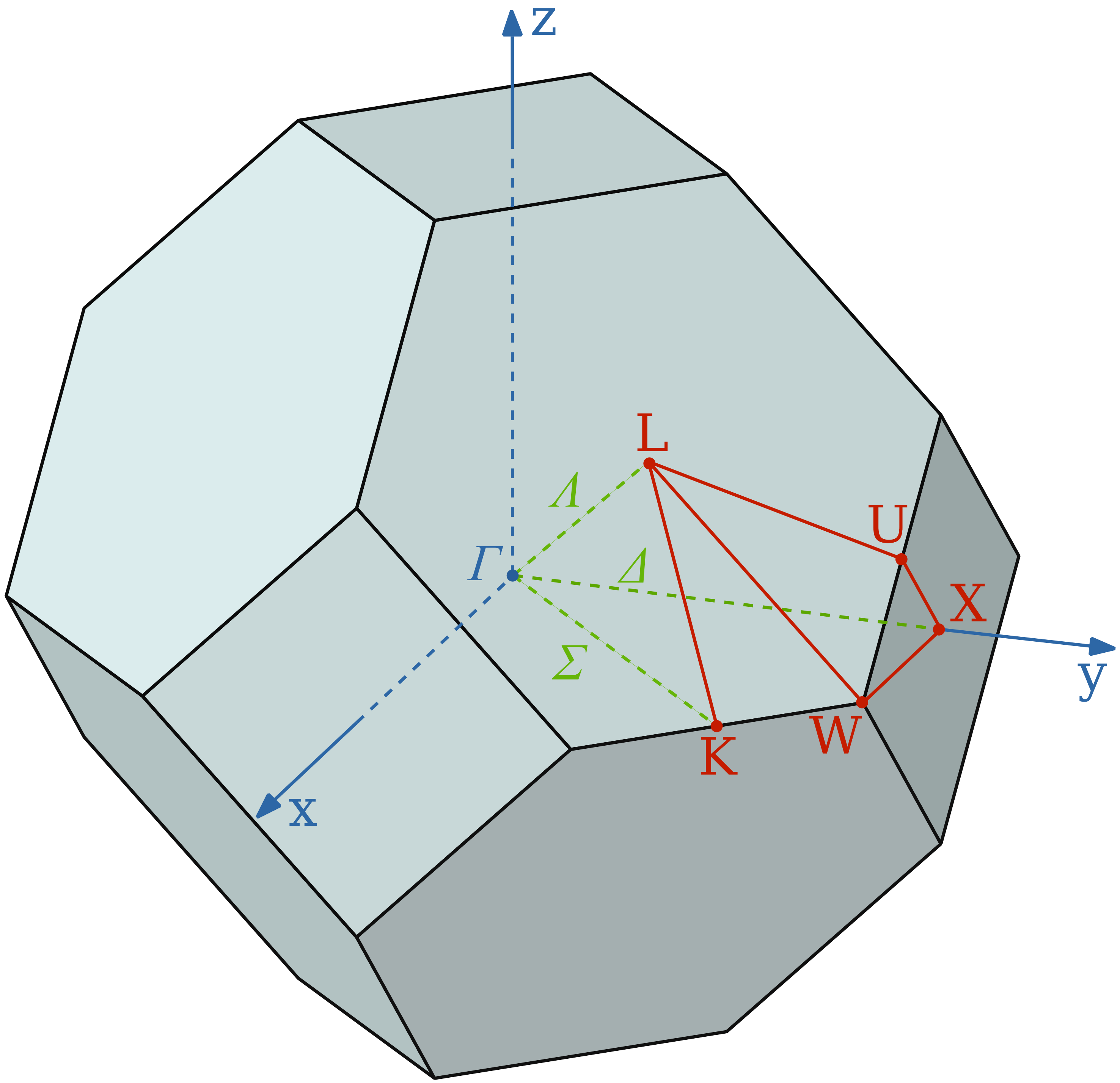
Optical Selection Rules

Character Table and Bases for the Cubic Group O_h

Repr.	Basis	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	i	$3iC_4^2$	$6iC_4$	$6iC_2$	$8iC_3$
Γ_1	1	1	1	1	1	1	1	1	1	1	1
Γ_2	$x^4(y^2-z^2)+$ $y^4(z^2-x^2)+$ $z^4(x^2-y^2)$	1	1	-1	-1	1	1	1	-1	-1	1
Γ_{12}	x^2-y^2 $2z^2-x^2-y^2$	2	2	0	0	-1	2	2	0	0	-1
Γ'_{15}	$xy(x^2-y^2)$ $yz(y^2-z^2)$ $zx(z^2-x^2)$	3	-1	1	-1	0	3	-1	1	-1	0
Γ'_{25}	xy, yz, zx	3	-1	-1	1	0	3	-1	-1	1	0
Γ'_1	$xyz[x^4(y^2-z^2)+$ $y^4(z^2-x^2)+$ $z^4(x^2-y^2)]$	1	1	1	1	1	-1	-1	-1	-1	-1
Γ'_2	xyz	1	1	-1	-1	1	-1	-1	1	1	-1
Γ'_{12}	$xyz(x^2-y^2)$ $xyz(2z^2-x^2-y^2)$	2	2	0	0	-1	-2	-2	0	0	1
Γ_{15}	x, y, z	3	-1	1	-1	0	-3	1	-1	1	0
Γ_{25}	$z(x^2-y^2)$ $x(y^2-z^2)$ $y(z^2-x^2)$	3	-1	-1	1	0	-3	1	1	-1	0

the em field transforms like Γ_{15}

The fcc Brillouin zone



Point/ line	Coordinate	Symmetry
Γ	$(0,0,0)$	O_h
L	$\pi/a(1,1,1)$	D_{3d}
X	$(2\pi/a,0,0)$	D_{4h}
K	$3\pi/a(1,1,0)$	C_{2v}
Δ	$(k_x,0,0)$	C_{4v}
Λ	$k(1,1,1)$	C_{3v}
Σ	$k(1,1,0)$	C_{2v}

Optical Selection Rules

PHYSICAL REVIEW B VOLUME 21, NUMBER 12 15 JUNE 1980

Dipole selection rules for optical transitions in the fcc and bcc lattices

W. Eberhardt
Department of Physics, and Laboratory for Research on the Stucture of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

F. J. Himpsel
Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, Wisconsin 53589

(Received 10 September 1979)

We present the compilation of dipole selection rules for all high-symmetry points and lines of the fcc and bcc lattices, which can be used for the interpretation of absorption or photoemission data in the one-electron direct-transition picture.

Optical Selection Rules

O_h	Γ_1	Γ_2	Γ_{12}	$\Gamma_{15'}$	$\Gamma_{25'}$	$\Gamma_{1'}$	$\Gamma_{2'}$	$\Gamma_{12'}$	Γ_{15}	Γ_{25}
Γ_1	···	···	···	···	···	···	···	···	+	···
Γ_2	···	···	···	···	···	···	···	···	···	+
Γ_{12}	···	···	···	···	···	···	···	···	+	+
$\Gamma_{15'}$	···	···	···	···	···	+	···	+	+	+
$\Gamma_{25'}$	···	···	···	···	···	···	+	+	+	+
$\Gamma_{1'}$	···	···	···	+	···	···	···	···	···	···
$\Gamma_{2'}$	···	···	···	···	+	···	···	···	···	···
$\Gamma_{12'}$	···	···	···	+	+	···	···	···	···	···
Γ_{15}	+	···	+	+	+	···	···	···	···	···
Γ_{25}	···	+	+	+	+	···	···	···	···	···

Optical Selection Rules

TABLE III. Allowed dipole transitions at Δ. $(+)$ is for $\vec{A}$ parallel Δ; $\vec{A}\cdot\vec{p}$ is represented by Δ_1. (0) is for $\vec{A}$ normal Δ; $\vec{A}\cdot\vec{p}$ is represented by Δ_5.

C_{4v}	Δ_1	$\Delta_{1'}$	Δ_2	$\Delta_{2'}$	Δ_5
Δ_1	+	···	···	···	0
$\Delta_{1'}$	···	+	···	···	0
Δ_2	···	···	+	···	0
$\Delta_{2'}$	···	···	···	+	0
Δ_5	0	0	0	0	+

TABLE IV. Allowed dipole transitions at Σ, D, G, K, U, S, and Z. $(+)$ is for $\vec{A}$ parallel Σ; $\vec{A}\cdot\vec{p}$ is represented by Σ_1. (0) is for $\vec{A}$ normal Σ, parallel x; $\vec{A}\cdot\vec{p}$ is represented by Σ_3. (X) is for $\vec{A}$ normal Σ, parallel y; $\vec{A}\cdot\vec{p}$ is represented by Σ_4.

C_{2v}	Σ_1	Σ_2	Σ_3	Σ_4
Σ_1	+	···	0	X
Σ_2	···	+	X	0
Σ_3	0	X	+	···
Σ_4	X	0	···	+

Optical Selection Rules

TABLE VII. Allowed dipole transitions at X. (+) is for $\vec{A}$ parallel Δ; $\vec{A}\cdot\vec{p}$ is represented by $X_{4'}$. (0) is for $\vec{A}$ normal Δ; $\vec{A}\cdot\vec{p}$ is represented by $X_{5'}$.

D_{4h}	X_1	X_2	X_3	X_4	$X_{1'}$	$X_{2'}$	$X_{3'}$	$X_{4'}$	X_5	$X_{5'}$
X_1	...	...	...	...	...	...	...	+	...	0
X_2	...	...	...	...	...	...	+	...	...	0
X_3	...	...	...	...	...	+	...	...	...	0
X_4	...	...	...	...	+	...	...	...	...	0
$X_{1'}$	...	...	...	+	...	...	...	...	0	...
$X_{2'}$	...	...	+	...	...	...	...	...	0	...
$X_{3'}$	...	+	...	...	...	...	...	...	0	...
$X_{4'}$	+	...	...	...	...	...	...	...	0	...
X_5	...	...	...	...	0	0	0	0	...	+
$X_{5'}$	0	0	0	0	...	...	...	...	+	...