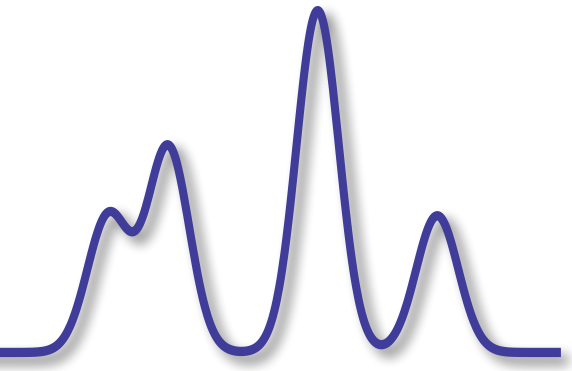
Symétrie



PHS 3210 - Spectroscopie

Chapitre 3

Invariance generates degeneracies

Noether's theorem

The invariance of the Hamiltonian under a continuous transformation leads to a conservation law.

Translational invariance $H(r) = H(r + \delta r)$ Conservation of momentum

Rotational invariance $H(\theta, \phi) = H(\theta + \delta\theta, \phi + \delta\phi)$ Conservation of angular momentum

Time invariance $H(t) = H(t + \tau)$ Conservation of energy

no spin-orbit interaction

Discrete rotational invariance: an object with rotational symmetry

RI

Discrete translational invariance: periodic potential

$H(\boldsymbol{r} + \boldsymbol{R}) = H(\boldsymbol{r})$ leads to Bloch's theorem $\psi(\boldsymbol{r} + \boldsymbol{R}) = e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\psi(\boldsymbol{r})$

Periodic lattice vector

Periodic potential + rotational invariance:

Symmetry operation S

$H(S^{-1}\boldsymbol{r}) = H(\boldsymbol{r})$ leads to $\psi_{n,\boldsymbol{k}}(S^{-1}\boldsymbol{r})$ being degenerate with $\psi_{n,\boldsymbol{k}}(\boldsymbol{r})$

and $E_n(S\boldsymbol{k}) = E_n(\boldsymbol{k})$

Periodic potential + time reversal invariance:

leads to $\psi_{n,\boldsymbol{k}}(\boldsymbol{r}, t)$ being degenerate with $\psi^*_{n,\boldsymbol{k}}(\boldsymbol{r}, -t)$

to $\psi^*_{n,\boldsymbol{k}}(\boldsymbol{r}) = \psi_{n,-\boldsymbol{k}}(\boldsymbol{r})$ and to $E_n(-\boldsymbol{k}) = E_n(\boldsymbol{k})$

Importance de la symétrie

Les éléments de symétrie d'un objet, peu importe sa nature ou son origine, forment toujours un groupe.

La théorie des groupes est un puissant **outil algébrique** permettant d'analyser un système physique présentant des relations de symétrie. Cette théorie est très importante en physique et, particulièrement, en mécanique quantique.

La symétrie

- détermine de nombreuses propriétés d'un système
- simplifie les calculs
- régit l'interaction d'un système avec la lumière
- révèle des connexions entre des phénomènes disparates

Exemple: La symétrie nous aide à déterminer

- les propriétés de la fonction d'onde
- les modes de vibration d'une molécule ou d'un solide
- l'existence de dégénérescences
- si une transition entre deux niveaux est permise

Objectif

Défi

$$\langle \psi_f | \hat{O} | \psi_i \rangle$$

operator

final state

initial state

À l'aide de la théorie des gà l'aide de propriétés de transformation des opérateurs et des fonctions d'ondes. Ces dernières sont exprimées dans les tables des caractères.

D_{3h}	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
A'_1	1	1	1	1	1	1
A'_2	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A''_1	1	1	1	-1	-1	-1
A''_2	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

Calculation of integrals

operator

$$\langle \psi_f | \hat{O} | \psi_i \rangle$$

final state *initial state*

Group theory will help us determine whether an integral is equal or different than zero.

Objectif

operator

$$\langle \psi_f | \hat{O} | \psi_i \rangle$$

final state

initial state

Les propriétés de transformation des opérateurs et des fonctions d'ondes suffiront à déterminer si une intégrale est nulle ou non-nulle.

Les propriétés de transformation d'un système de symétrie donné sont exprimés dans les tables des caractères.

D_{3h}	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
A'_1	1	1	1	1	1	1
A'_2	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A''_1	1	1	1	-1	-1	-1
A''_2	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

Group theory

Definition
Symmetry operations

The concept of groups

Definition

Given an ensemble formed from multiple elements $g_1, g_2, g_3, \ldots$. This ensemble forms a group, G, if the following four conditions are satisfied,

1. The *product* of any two elements belongs to this ensemble, $g_1 g_2 = g_3$

2. Associativity is respected for all elements, $(g_1 g_2) g_3 = g_1 (g_2 g_3)$

3. For all elements, there exists an identity elements, E, such that, $g_1 E = E g_1 = g_1$

4. For all elements, there exists an inverse element such that, $g_1 g_1^{-1} = g_1^{-1} g_1 = E$

Notes

- As operator between group elements, we use the multiplication.
- Associativity is in general not a constraint under multiplication.
- Commutativity is generally not respected.
- The multiplication table of a group expresses relationships between group elements

$\mathcal{G}_{(1\rightarrow,\,2\downarrow)}$	g_1	g_2	g_3	$\cdots$
g_1	g_1^2	$g_1 g_2$	$g_1 g_3$	$\cdots$
g_2	$g_2 g_1$	g_2^2	$g_2 g_3$	$\cdots$
g_3	$g_3 g_1$	$g_3 g_2$	g_3^2	$\cdots$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$

Permutation group P_3

Example

The group P_3 is formed from the 3! permutations of 3 objects.

Cauchy notation: top set is the initial configuration, bottom set expresses the permutation

$$p_1 = \begin{bmatrix} \square & \diamond & \triangle \\ \square & \diamond & \triangle \end{bmatrix} \quad p_2 = \begin{bmatrix} \square & \diamond & \triangle \\ \diamond & \triangle & \square \end{bmatrix} \quad p_3 = \begin{bmatrix} \square & \diamond & \triangle \\ \triangle & \square & \diamond \end{bmatrix}$$

$$p_4 = \begin{bmatrix} \square & \diamond & \triangle \\ \square & \triangle & \diamond \end{bmatrix} \quad p_5 = \begin{bmatrix} \square & \diamond & \triangle \\ \triangle & \diamond & \square \end{bmatrix} \quad p_6 = \begin{bmatrix} \square & \diamond & \triangle \\ \diamond & \square & \triangle \end{bmatrix}$$

The multiplication table is

$\mathcal{P}_3 (1 \rightarrow, 2 \downarrow)$	p_1	p_2	p_3	p_4	p_5	p_6
p_1	p_1	p_2	p_3	p_4	p_5	p_6
p_2	p_2	p_3	p_1	p_5	p_6	p_4
p_3	p_3	p_1	p_2	p_6	p_4	p_5
p_4	p_4	p_6	p_5	p_1	p_3	p_2
p_5	p_5	p_4	p_6	p_2	p_1	p_3
p_6	p_6	p_5	p_4	p_3	p_2	p_1

1) The group is closed
3) There is an identity for all elements
4) There is an inverse for all elements
-> This is a group!

A few useful definitions

Definitions

- The order of a group G is given by the number of elements, *h.*

- If a subset of elements of G also form a group, then this subset H is a subgroup of G. The order of H is a divisor of the order of G.

- The order of an element g is defined by the smallest integer *n* such that g^n=E. {g, g^2,..., g^n} is a sub-group of G.

- If all elements of the group G can be generated from the powers of g, the group is said to by cyclic.

- Two elements of G, g_i and g_j are conjugate, if a third element g_k exists such that

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

- All conjugate elements can be grouped in classes K_i. The element of the group can be expressed as a sum of classes,

$$\mathcal{G} = \{\mathcal{K}_1, \mathcal{K}_2, \mathcal{K}_3, \ldots\}$$

P_3 example

h=6

$$\{p_1, p_2, p_3\}, \{p_1, p_4\}, \{p_1, p_5\}, \{p_1, p_6\}$$

The order of p_1, p_2, p_3, p_4, p_5, p_6 are 1, 3, 3, 2,2, 3

$$\{p_1, p_2, p_3\},$$

is cyclic. p_2 generates all three elements. Also the case for p_3.

p_2 and p_3 are conjugate
p_4,p_5, and p_6 are mutually conjugates

K_1= p_1
K_2= p_2, p_3
K_3= p_4, p_5, p_6

… and a few more…

Definitions

- If all elements commute, the group is abelian. Abelian groups have as many classes as elements.

- Reorganization theorem: If G= {E, g_1, g_2, …., g_n}, then the ensemble g_i{E, g_1, g_2, …., g_n}={g_iE, g_ig_1, g_ig_2, …., g_i g_n} contains all elements and only once.

- A complex is an ensemble where the same element can appear more than once.

- Dyadic product of two complexes is a complex,

$$\mathcal{A} \odot \mathcal{B} = \{a_1b_1, a_1b_2, \ldots, a_nb_1, a_nb_2, \ldots\}$$

- Scalar product is a dyadic product for which duplicate elements are omitted

- The dyadic product of two classes can always be expressed as a sum of classes

$$\mathcal{K}_i \odot \mathcal{K}_j = \sum_k c_{ijk}\mathcal{K}_k$$

Always an integer

P_3 example

Not abelian.

This explains why rows and columns of the multiplication table contains each element once.

$$\mathcal{A} = \{p_1, p_2, p_2, p_3, p_1, p_4, p_5\}.$$

$$\mathcal{H} = \{p_1, p_2, p_3\}$$
$$\mathcal{F} = \{p_4, p_5, p_6\}$$
$$\mathcal{H} \odot \mathcal{F} = \{p_4, p_5, p_6, p_5, p_6, p_4, p_6, p_4, p_5\}$$

$$\mathcal{H} \cdot \mathcal{F} = \{p_4, p_5, p_6\}$$

$$\mathcal{K}_1 = \{p_2, p_3\} \qquad \mathcal{K}_2 = \{p_4, p_5, p_6\}$$

$$\begin{aligned}\mathcal{K}_1 \odot \mathcal{K}_2 &= \{p_5, p_6, p_4\} + \{p_6, p_4, p_5\} \\ &= \{2p_4, 2p_5, 2p_5\} \\ &= 2\{p_4, p_5, p_5\} \\ &= 0\mathcal{K}_1 + 2\mathcal{K}_2\end{aligned}$$

Isomorphism between two groups

Definitions

Two groups of the same order, G and H, are isomorphic if there exists a one-to-one correspondence between their elements

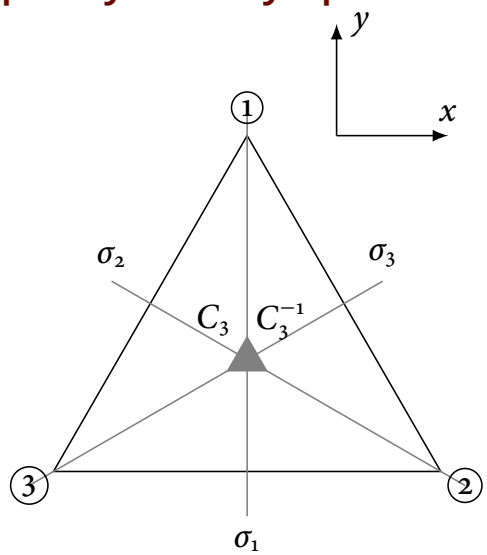
$$(g_1 \leftrightarrow h_1, g_2 \leftrightarrow h_2, \ldots)$$

and if the same interrelations exist in both groups,

$$\text{if} \quad g_1 g_2 = g_3 \qquad \text{then} \quad h_1 h_2 = h_3$$

Example: symmetry operation of an equilateral triangle

2D	Identité	E
	Rotation de $2\pi/n$ selon l'axe z	C_n
	Plan miroir défini par la normale i	σ_i



D_3 $(1 \rightarrow, 2 \downarrow)$	E	C_3	C_3^{-1}	σ_1	σ_2	σ_3
E	E	C_3	C_3^{-1}	σ_1	σ_2	σ_3
C_3	C_3	C_3^{-1}	E	σ_2	σ_3	σ_1
C_3^{-1}	C_3^{-1}	E	C_3	σ_3	σ_1	σ_2
σ_1	σ_1	σ_3	σ_2	E	C_3^{-1}	C_3
σ_2	σ_2	σ_1	σ_3	C_3	E	C_3^{-1}
σ_3	σ_3	σ_2	σ_1	C_3^{-1}	C_3	E

$$p_1 \leftrightarrow E \qquad p_2 \leftrightarrow C_3 \qquad p_3 \leftrightarrow C_3^{-1}$$
$$p_4 \leftrightarrow \sigma_{v,1} \qquad p_5 \leftrightarrow \sigma_{v,2} \qquad p_6 \leftrightarrow \sigma_{v,3}$$

P_3 and D_3 are isomorphic

Point groups

Definition
Symmetry operations
Schöflies notation

Point groups

Definition Group of symmetry operations leaving one point of space fixed.

Most relevant for systems lacking translational symmetry, like molecules or crystals with a single defect.

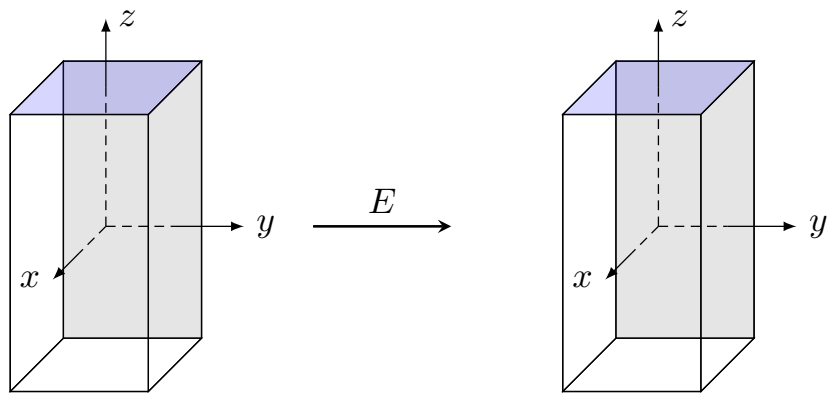
Operations to consider

	Élément	Notation
3D	Identité	E
	Inversion	I
	Rotation de $2\pi/n$ selon l'axe i	$C_n^{(i)}$
	Plan miroir défini par la normale i	σ_i
	Rotoreflexion	$S_n^{(i)} = \sigma_i C_n^{(i)}$
2D	Identité	E
	Rotation de $2\pi/n$ selon l'axe z	C_n
	Plan miroir défini par la normale i	σ_i
1D	Identité	E
	Inversion	I

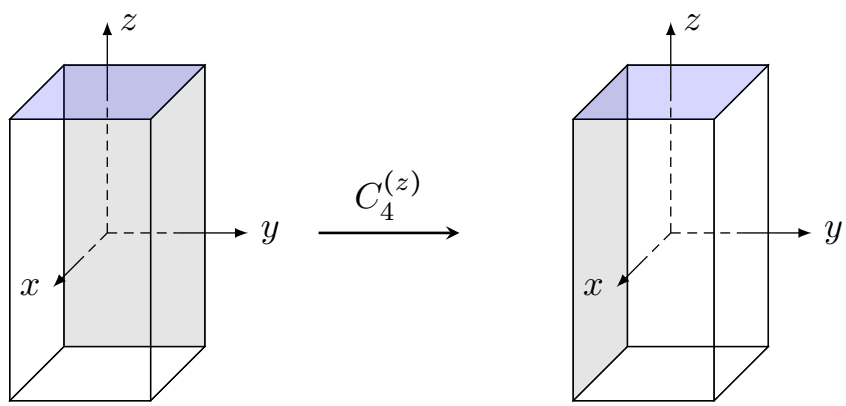
Proper rotations

Preserve handedness (det=1)

Identity operation



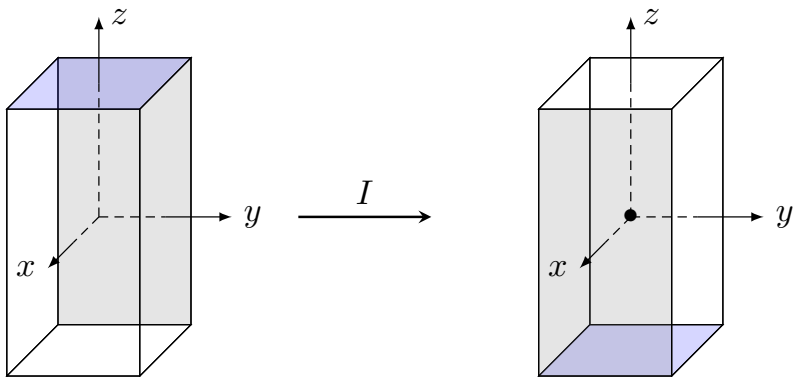
Rotation operations



Improper rotations

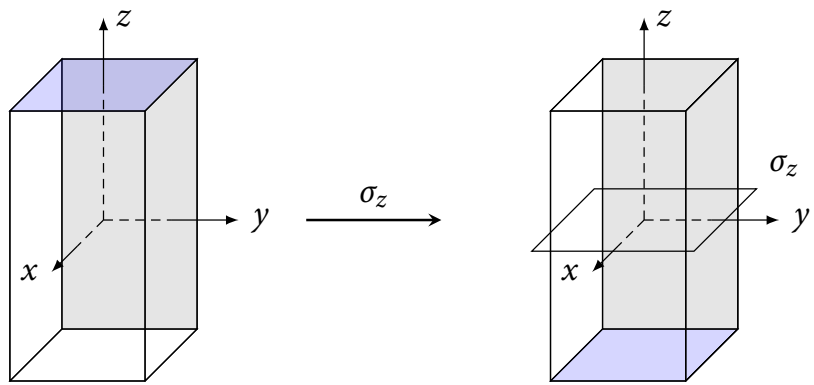
Reverse handedness (det=-1)

Inversion inversion



Improper rotations *Reverse handedness (det=-1)*

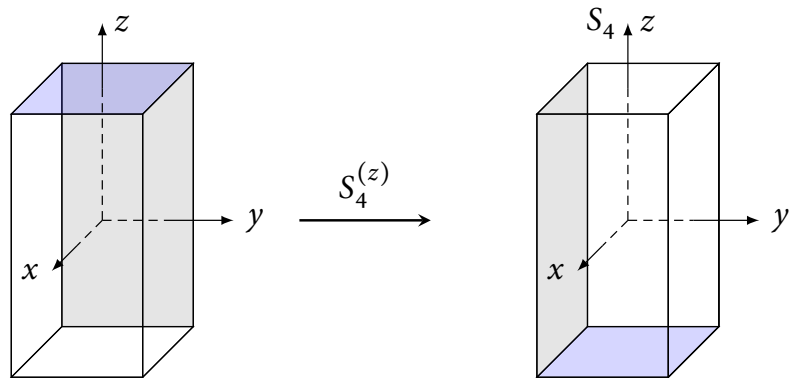
Reflection operations



Opération	Description
σ_h	Le plan miroir est ⊥ à l'axe de plus grande symétrie
σ_v	Le plan miroir contient l'axe de plus grande symétrie
σ_d	Un plan σ_v entre deux axes C_2 NOTE: lorsqu'il existe 2 familles de plan σ_v, on utilise parfois σ_d pour représenter le plan qui passe majoritaire ment entre les atomes

Improper rotations *Reverse handedness (det=-1)*

Rotoflections A rotation followed by a mirror plane



Note: n>2

$$S_1 = \sigma_h$$

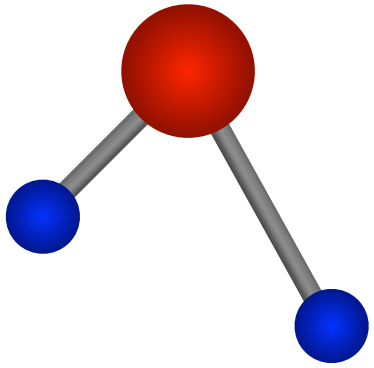
$$S_2 = I$$

Exemple: H_20

On cherche les éléments de symétrie laissant la molécule H_20 dans une configuration ***indiscernable*** de la configuration initiale.

La configuration d'une molécule est définie par les positions des noyaux atomiques, car ce sont eux qui déterminent la forme du potentiel que l'on retrouve dans l'hamiltonien. On suppose ces noyaux stationnaires.

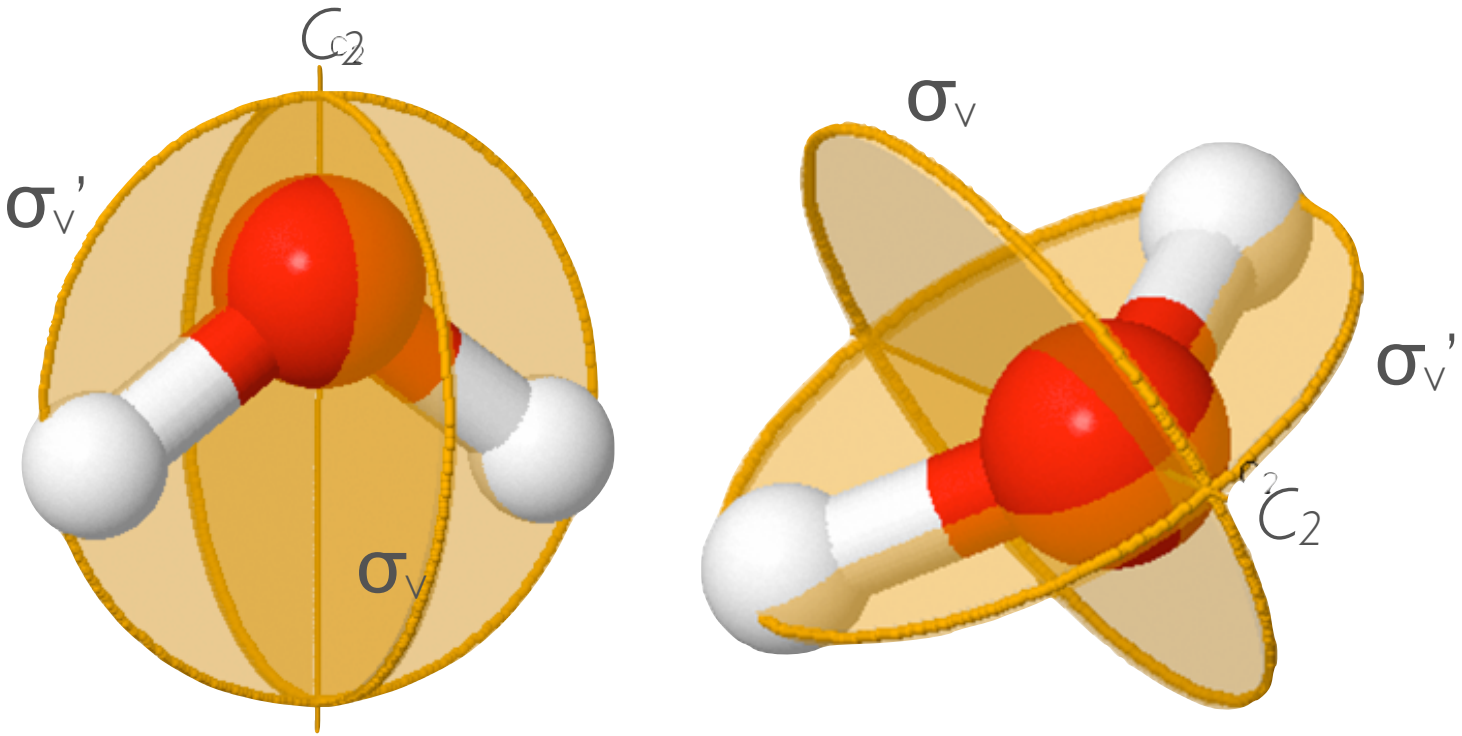
Considérons systématiquement tous les éléments de symétrie des groupes ponctuels compatibles avec la molécule H_20.



Exemple: H_20

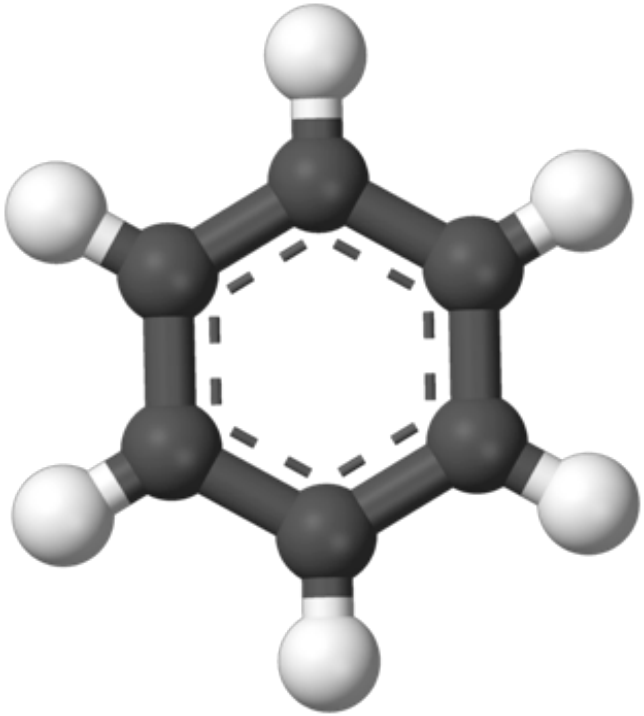
Les opérations lassant la molécule dans une configuration indiscernable

$$E,\ C_2,\ \sigma_v,\ \sigma_v'$$



Par convention, le plan miroir **σ** *est perpendiculaire au plan de la molécule.*

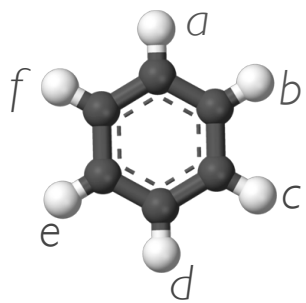
Exemple: Benzène



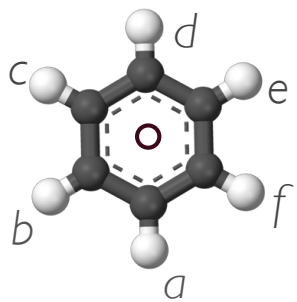
Exemple: Benzène

Voici les éléments de symétrie de la molécule de benzène.

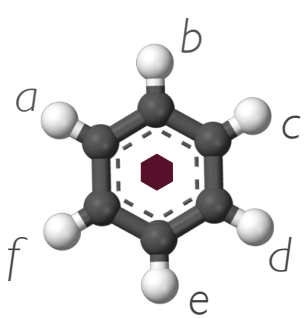
1) E ? Bien sûr

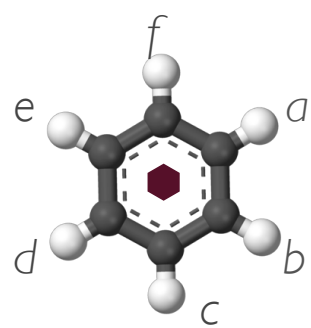


2) I ? Oui



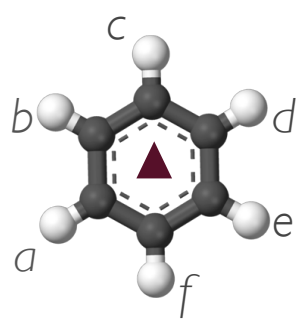
3) C_6 ? 2x

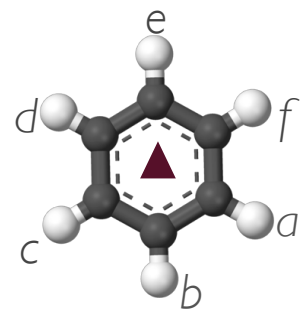




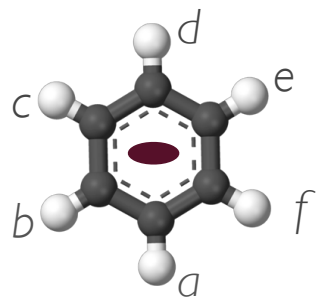
Exemple: Benzène

4) C_3 ? 2x



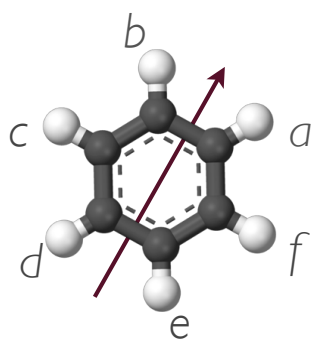


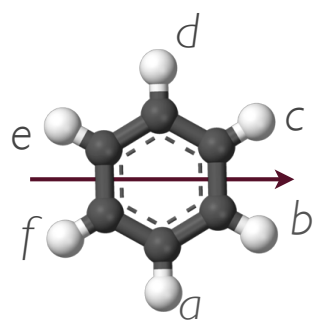
5) C_2? Oui

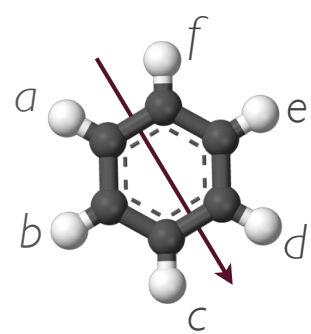


Note: C_2^{-1} est la même opération que C_2. On ne considère qu'une seule de ces deux opérations.

6) C'_2 ? 3x

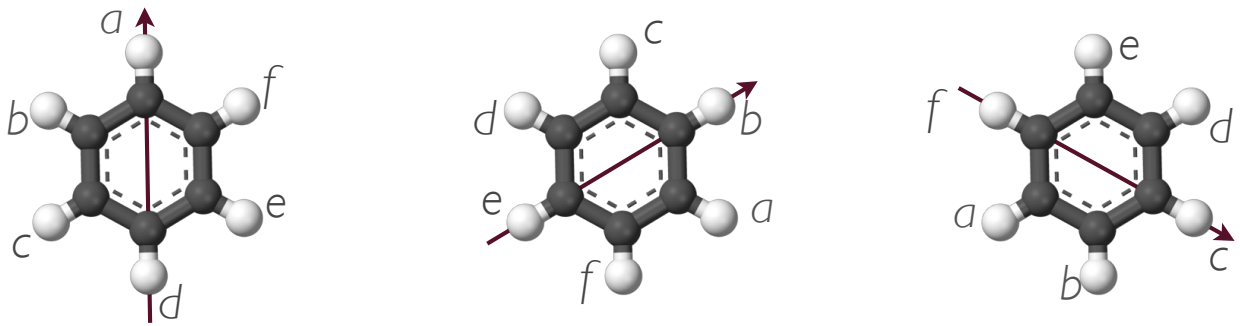






Exemple: Benzène

7) C''_2 ? 3x

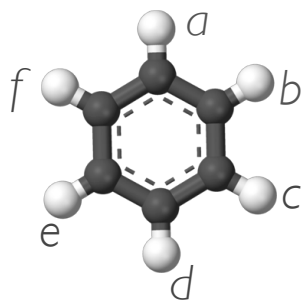


8) S_6? 2x

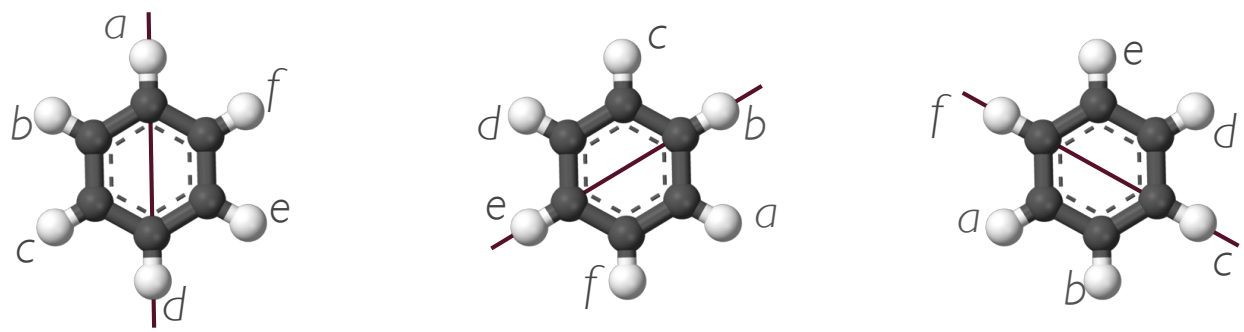
9) S_3 ? 2x

Exemple: Benzène

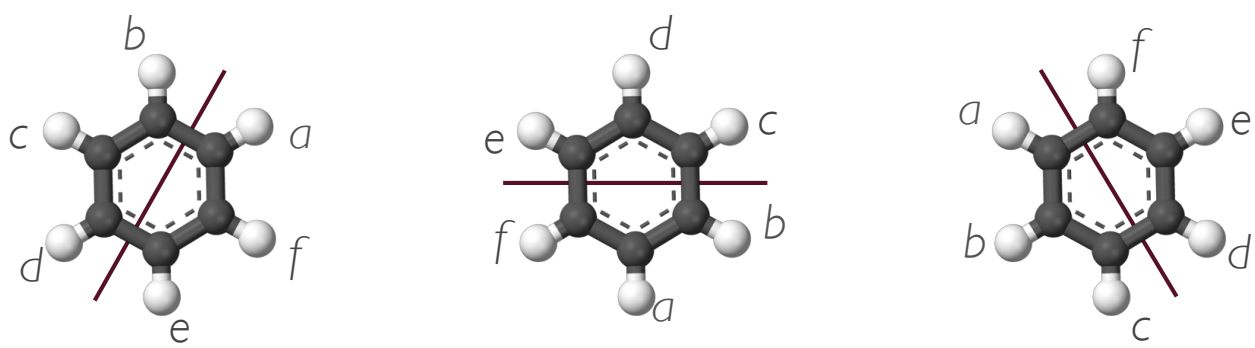
10) σ_h ? Une fois



11) σ_d ? 3x



12) σ'_d ? 3x

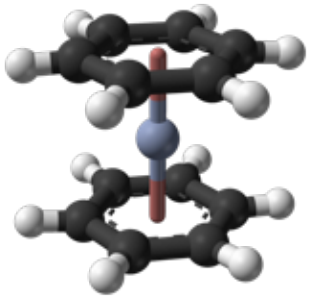


Exemple: Benzène

Nous avons ainsi 24 éléments de symétrie.

On remarque que certains éléments produisent des configurations identiques (par exemple E et σ_h). Il s'agit de coïncidences spécifiques à la molécule, car ces opérations sont fondamentalement différentes. Nous gardons donc ces 24 éléments pour obtenir un ensemble formant un groupe.

Par exemple, si la molécule n'avait pas été planaire, les configurations obtenues auraient été différentes pour chacun des éléments de symétrie.



Question

En énumérant la configuration indiscernable de boules colorées dans l'espace, que faisons-nous exactement?

Les classes

Les éléments conjugués sont souvent regroupés en classes, car ils possèdent des caractéristiques similaires.

Approche rigoureuse $g_j = g_k g_i g_k^{-1}$

g_i and g_j sont conjugué s'il existe g_k permettant de satisfaire cette relation.

Approche rapide

E et I forment toujours une classe composée d'un seul élément. C'est aussi souvent le cas pour σ_h.

C_n et C_n^{-1} appartiennent à la même classe s'il y a un σ_v ou un C_2 perpendiculaire à C_n. Ce principe s'applique aussi pour S_n et S_n^{-1}.

$C_{n,1}$ et $C_{n,2}$ appartiennent à la même classe si une opération du groupe permet de les superposer. Ce principe s'applique aussi pour σ_{v1} et σ_{v2}.

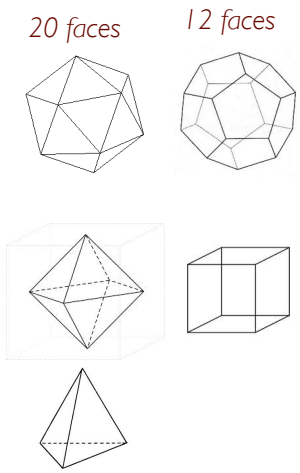
Ainsi pour la molécule de benzène:

$$E,\ I,\ 2C_6,\ 2C_3,\ C_2,\ 3C_2',\ 3C_2'',\ 2S_6,\ 2S_3,\ \sigma_h,\ 3\sigma_d,\ 3\sigma_d'$$

Note: parfois, pour on écrit σ_v pour σ_d et σ_d pour σ'_d

8. Notation de Schoenflies

Famille	Schoenflies	
Icosaèdre	I	Contient les opérations de symétrie d'un isocaèdre (20 faces) ou dodécaèdre (12 faces) - I : Contient des rotations d'ordre 5, 3 et 2 - I_h : Contient aussi des S6 et des S10
Octaèdre (cube)	O	Contient les opérations de symétrie d'un octaèdre ou d'un cube ($4C_4$, $3C_3$, $6C_2$) - O_h : inclut des rotoréflexions et un centre d'inversion
Tétraèdre	T	Contient les opérations de symétrie d'un tétraèdre ($4C_3$, $3C_2$). - T_d : inclut des rotoréflexion (S_4). - T_h : inclut aussi un centre d'inversion
Dièdre	D_n	Contient *n* rotations d'ordre 2 perpendiculaires à C_n - D_{nv} : inclut aussi *n* σ_v - D_{nh} : inclut aussi un σ_h
Spiegel (miroir)	S_n	Contient l'élément S_n.
Cyclique	C_n	Contient un axe de rotation C_n - C_{nv} : inclut *n* σ_v - C_{nh} : inclut un σ_h perpendiculaire à l'axe de rotation - C_i : n'inclut qu'un centre d'inversion



Rappel: projection stéréographique

Projection stéréographique

Pour construire une projection stéréographique, il faut

1. Placer l'objet 3D au centre d'une sphère, dans le plan équatorial. L'axe de plus grande symétrie doit coïncider avec l'axe N-S.
2. Tracer une ligne de l'origine (O) jusqu'à la surface de la sphère (P) en passant soit au centre d'une des faces de l'objet ou par la position des atomes. (Figure 3.14).
3. Si P est dans l'hémisphère nord, tracer ensuite une ligne de P jusqu'à S. Si P est dans l'hémisphère sud, tracer une ligne de P jusqu'au point N.
4. Répéter pour chacune des faces ou des liens atomiques, tel qu'illustré à la figure 3.15

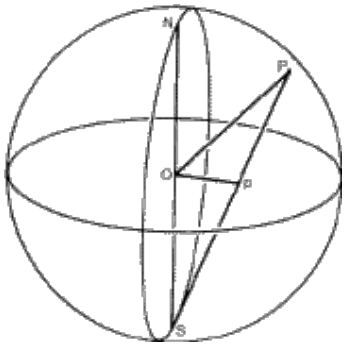
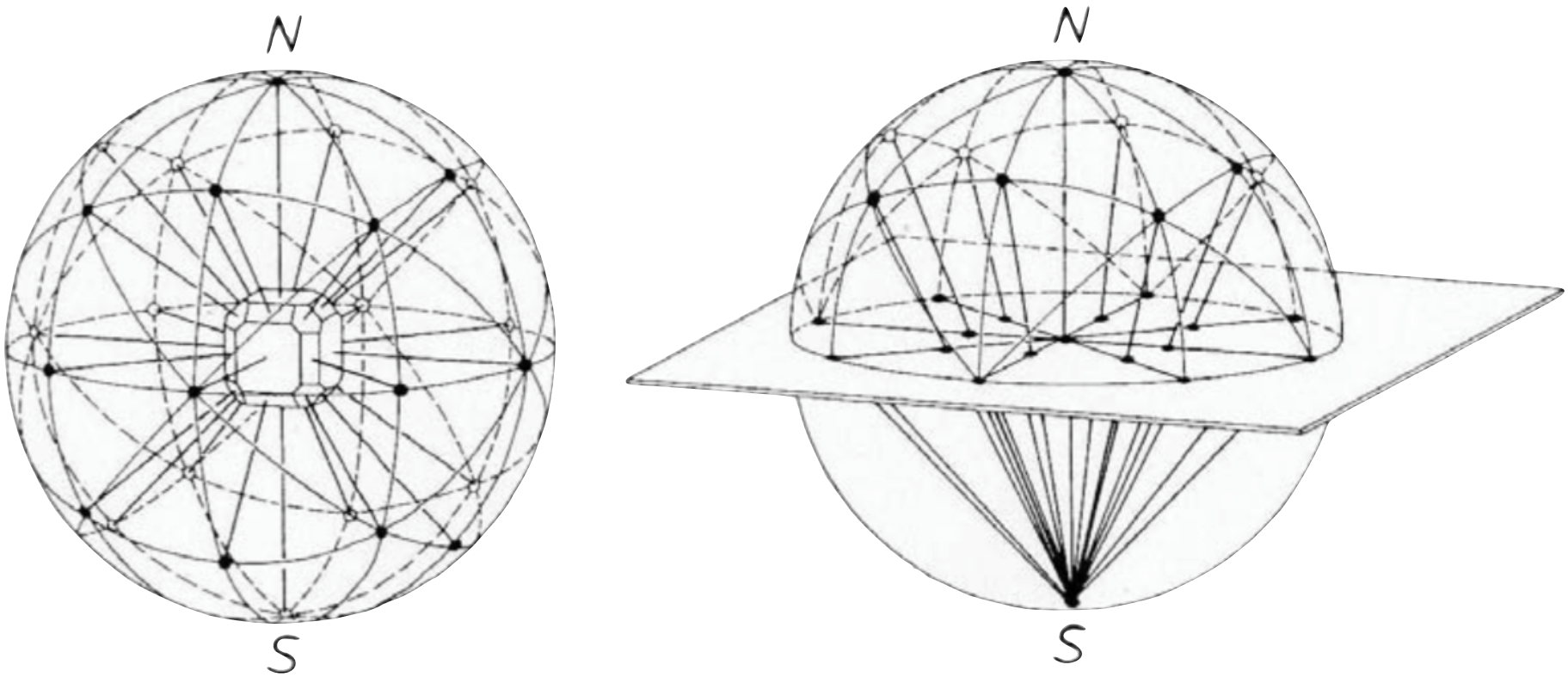


Figure 3.14: Les principes permettant de construire une projection stéréographique.

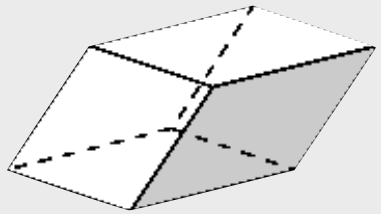
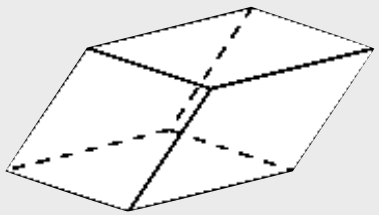
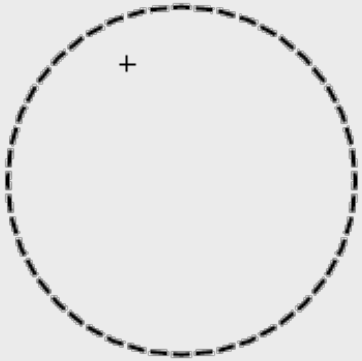
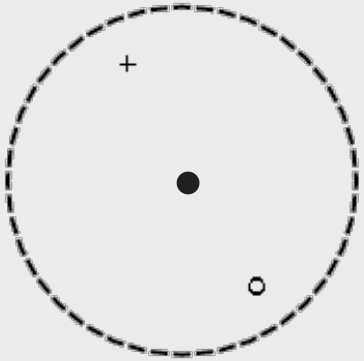
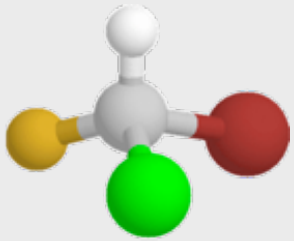
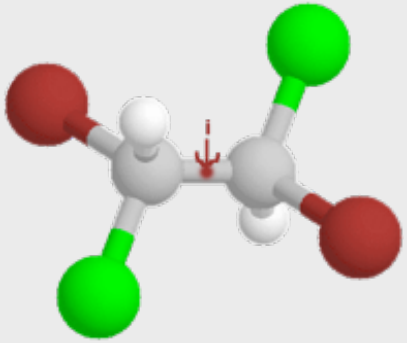
La projection stéréographique est donnée par tous les points formés par les intersections des tracés avec le plan équatorial. Si cette intersection provient de l'hémisphère nord (sud), celle-ci sera identifiée par un + (∘).

De façon tout à fait équivalente, il est possible de générer une projection stéréographique à partir des opérations de symétrie caractérisant un groupe.

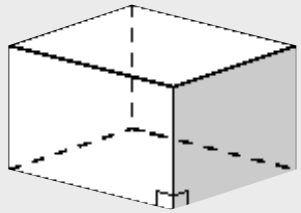
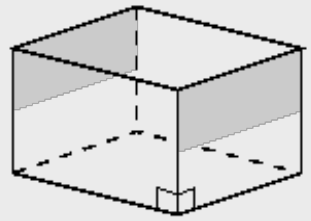
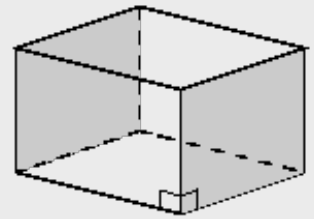
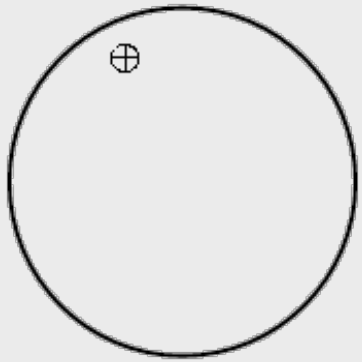
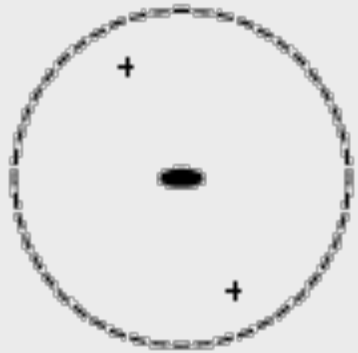
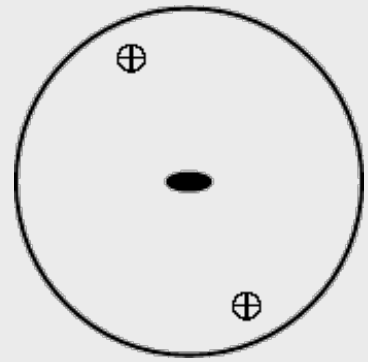
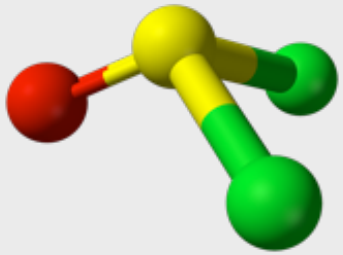
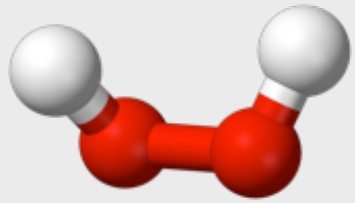
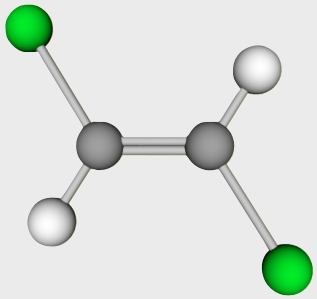
Rappel: projection stéréographique



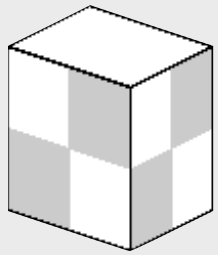
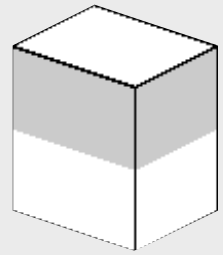
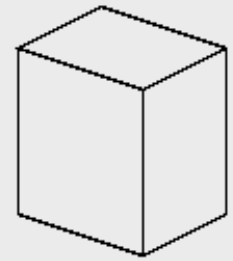
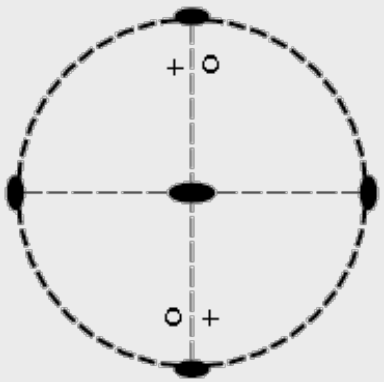
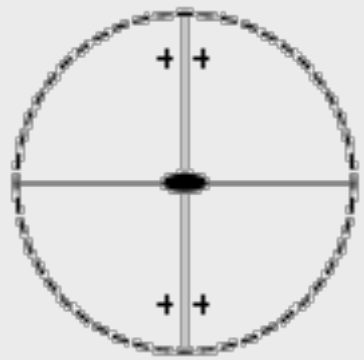
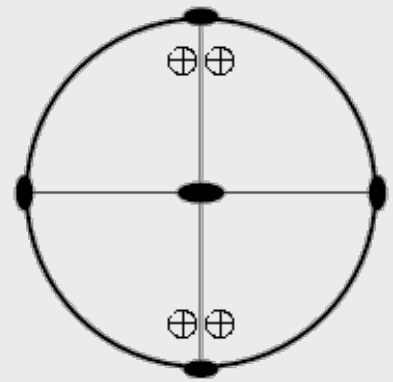
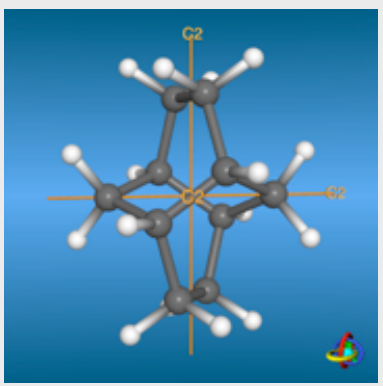
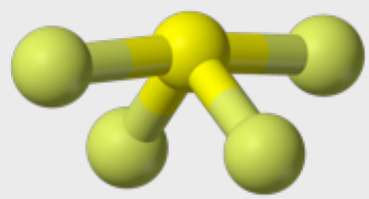
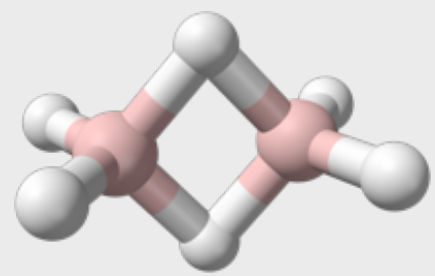
Les groupes ponctuels: Triclinique: C_1 et C_i

	C_1	C_i
Objet		
Proj. stéréo.		
Exemple	 CHFClBr	 HClBrC-CHClBr

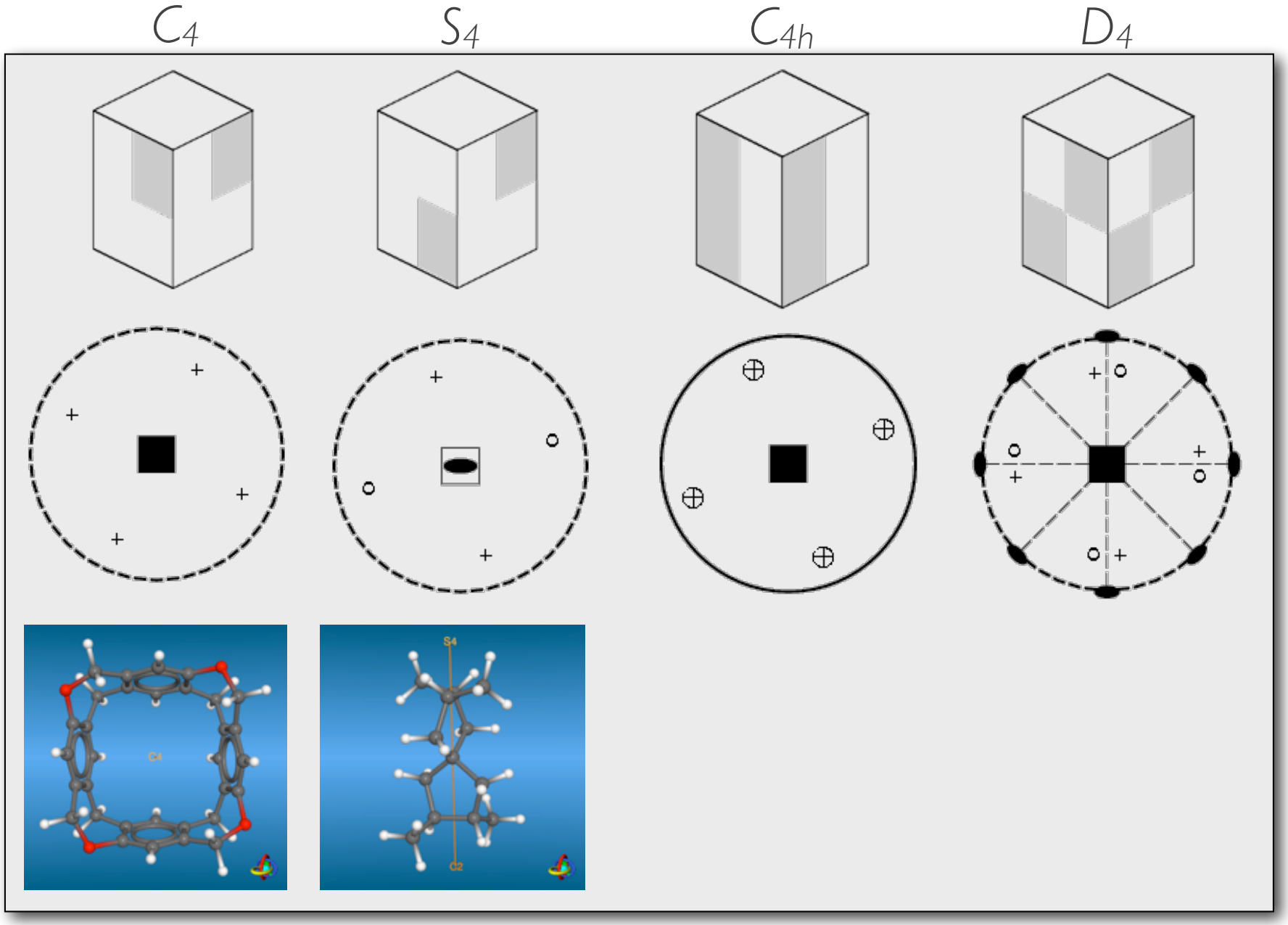
Monoclinique: C_s, C_2 et C_{2h}

	$C_s = C_{1h}$	C_2	C_{2h}
Objet			
Proj. stéréo.	 *plan miroir dans le plan de la page*	 *aucun plan miroir dans le plan de la page*	
Exemple	 $SOCl_2$	 H_2O_2	 trans-1,2-Dichloroethene

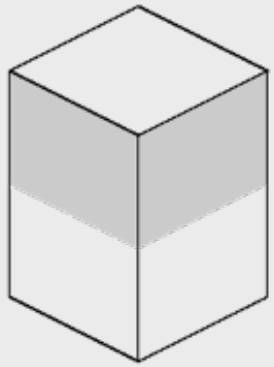
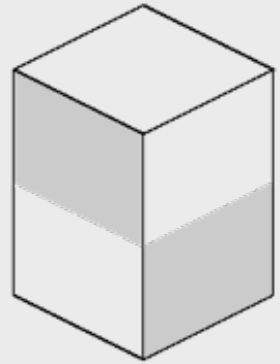
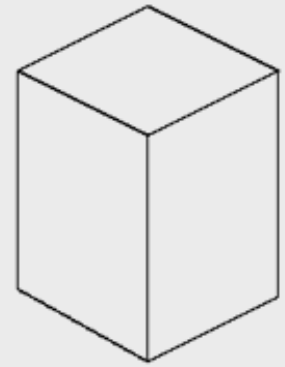
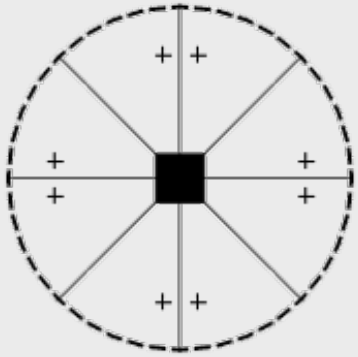
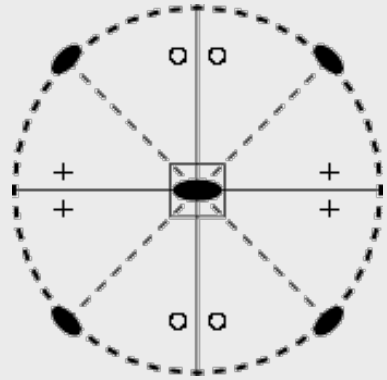
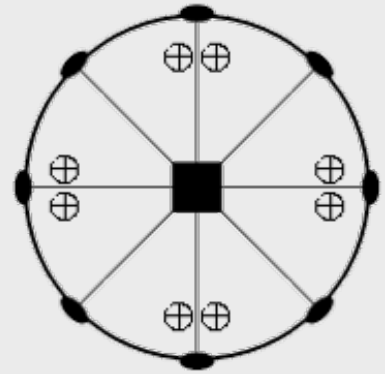
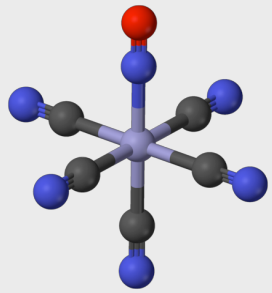
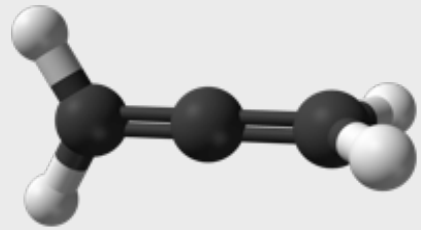
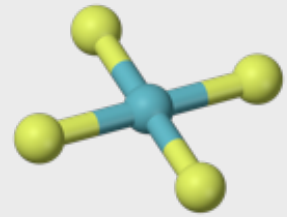
Orthorhombique: D_2, C_{2v} et D_{2h}

	D_2	C_{2v}	D_{2h}
Objet			
Proj. stéréo.			
Exemple		 SF_4	 B_2H_6

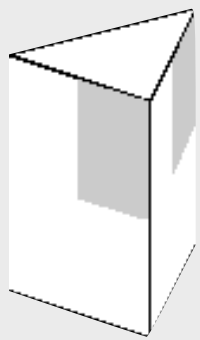
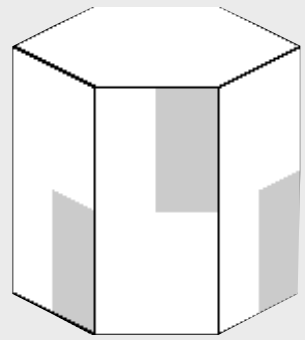
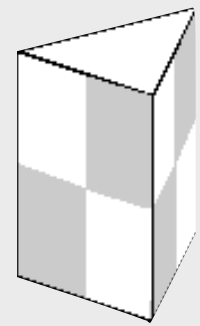
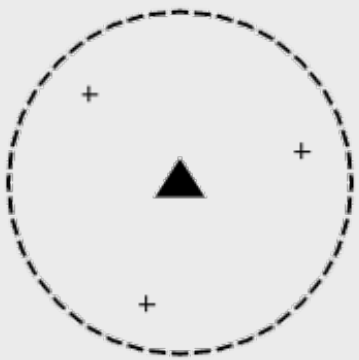
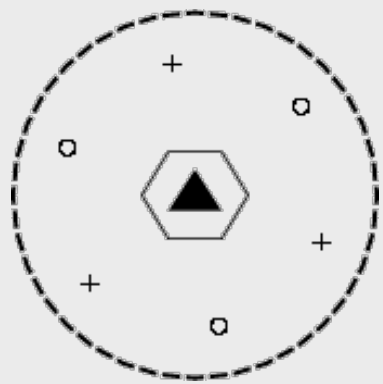
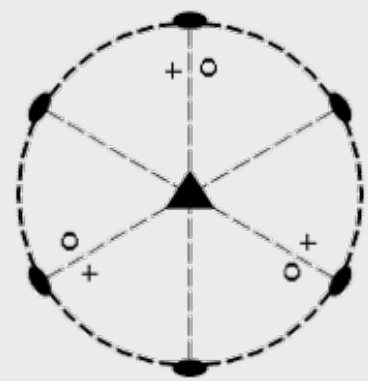
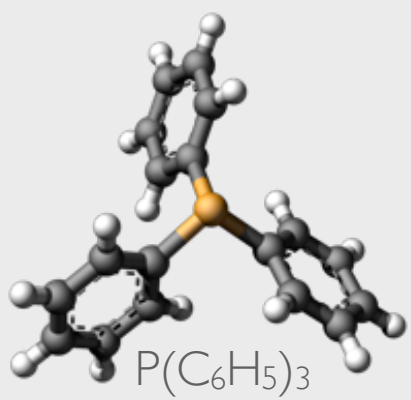
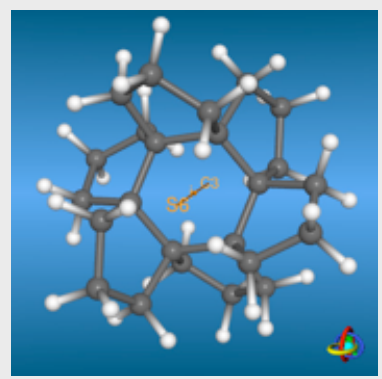
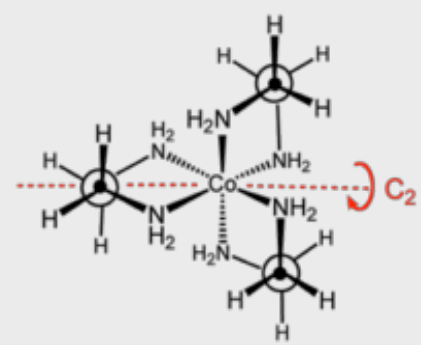
Tétragonal: C_4, S_4, C_{4h} et D_4



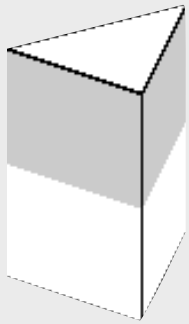
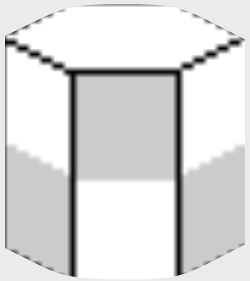
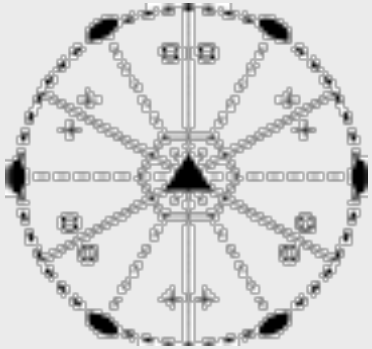
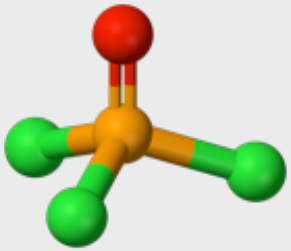
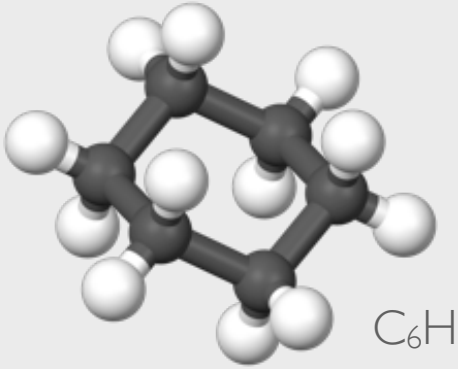
Tétragonal: C_{4v}, D_{2d}, et D_{4h}

	C_{4v}	D_{2d}	D_{4h}
Objet			
Proj. stéréo.			
Exemple	 $Fe(CN)_5NO$	 C_4H_3	 XeF_4

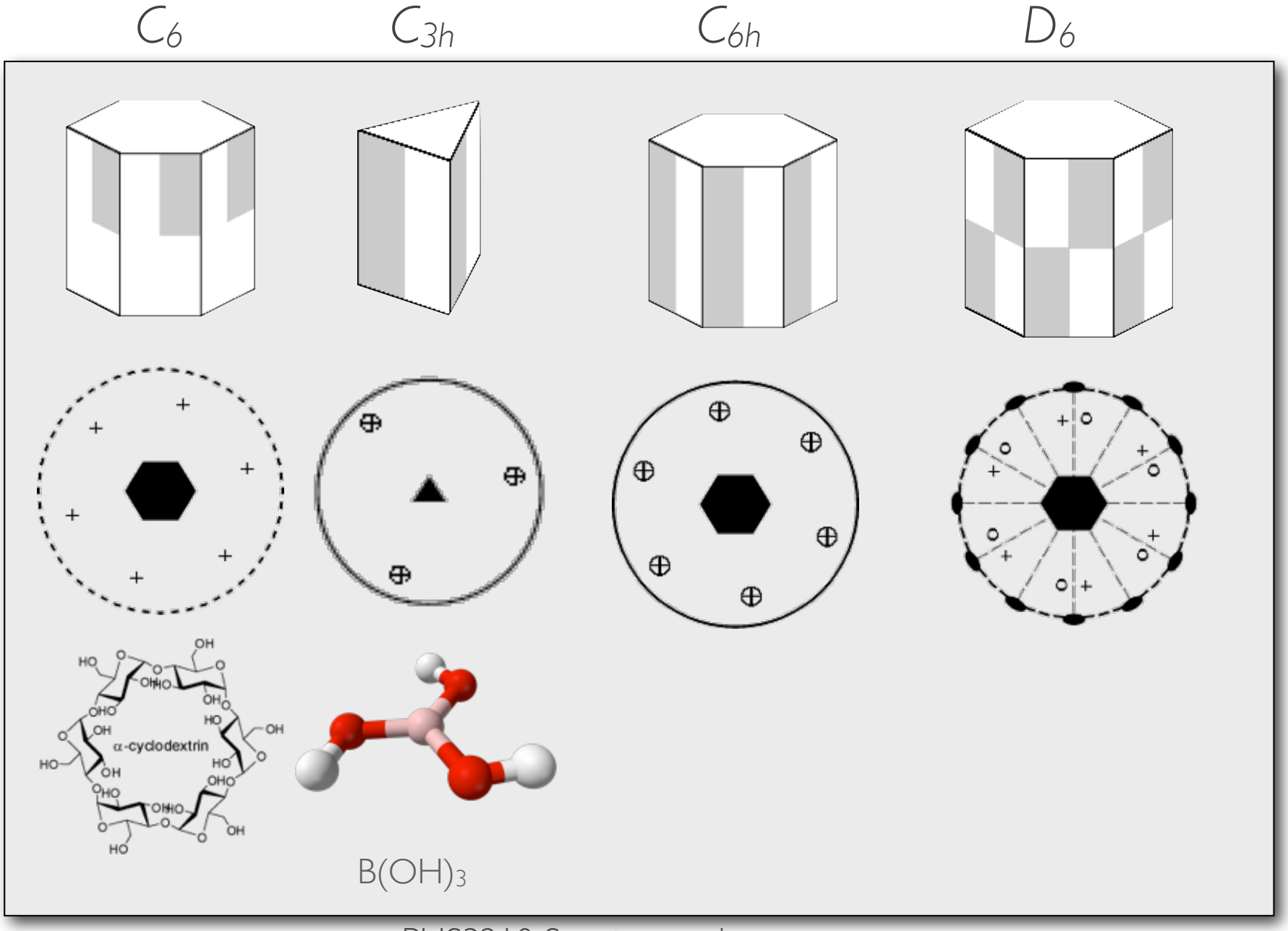
Trigonal: C_3, S_6 et D_3

	C_3	S_6	D_3
Objet			
Proj. stéréo.			
Exemple	 $P(C_6H_5)_3$		

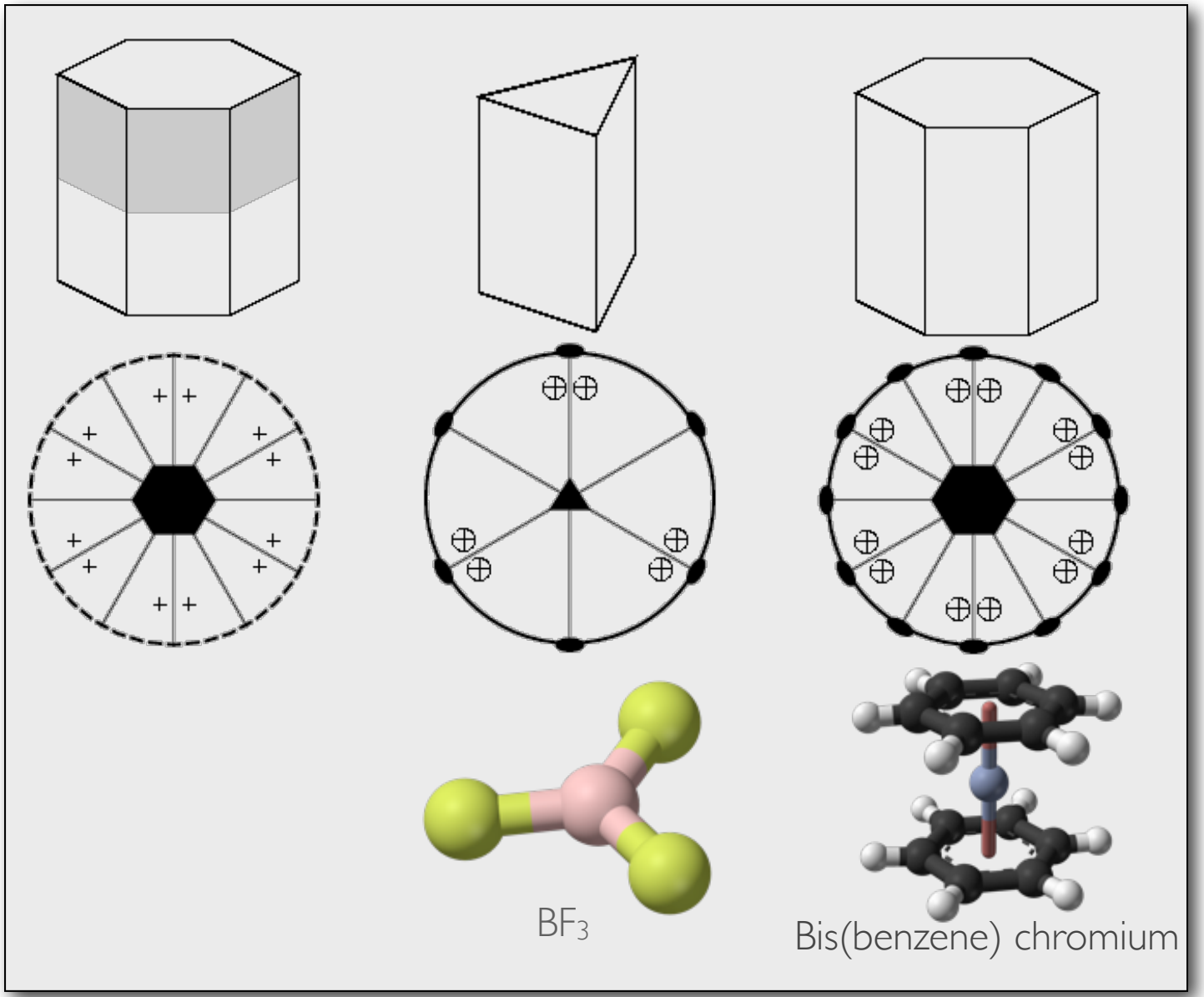
Trigonal: C_{3v} et D_{3d}

	C_{3v}	D_{3d}
Objet		
Proj. stéréo.		
Exemple	 $POCl_3$	 C_6H_{12}

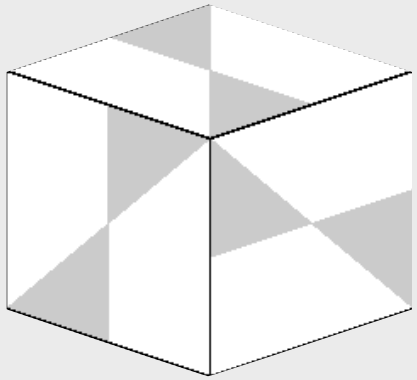
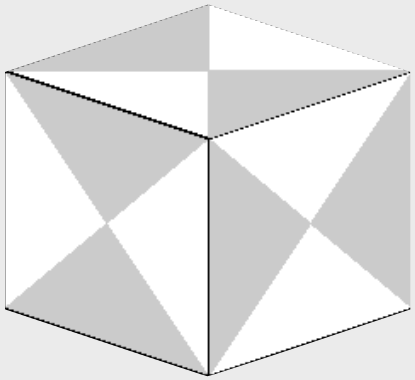
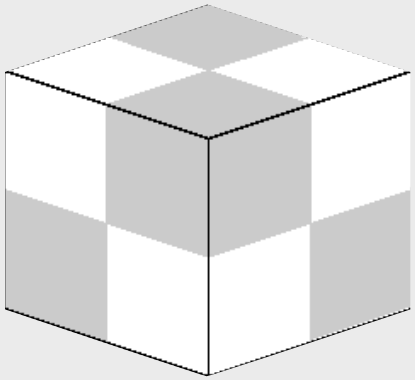
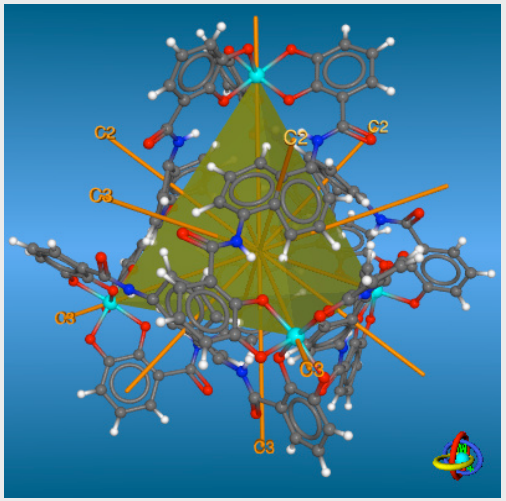
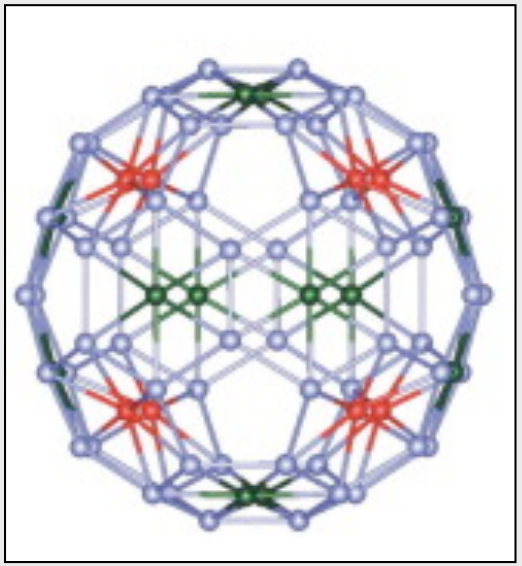
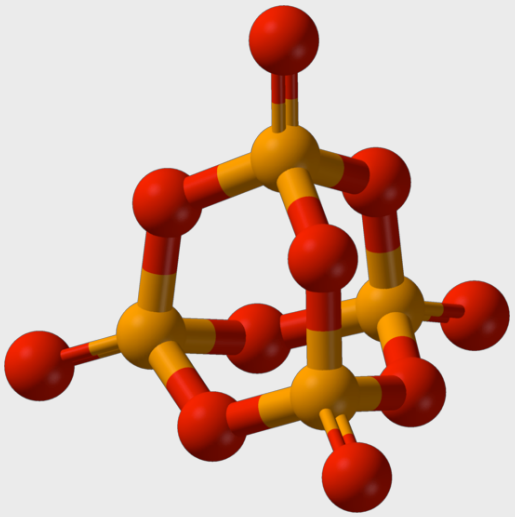
Hexagonal: C_6, C_{3h}, C_{6h}, et D_6



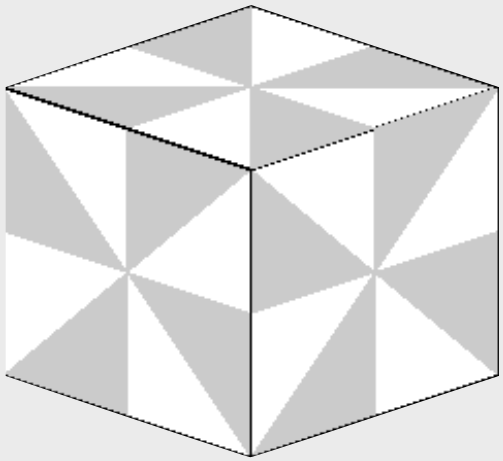
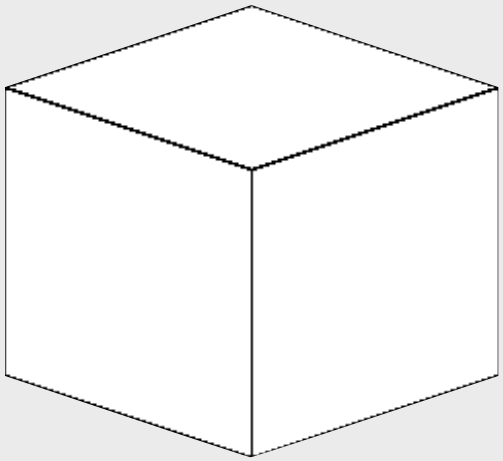
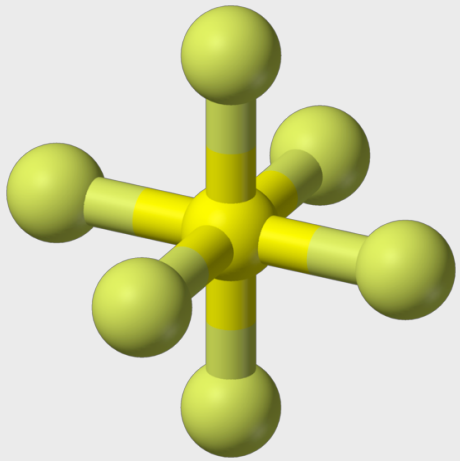
Hexagonal: C_{6v}, D_{3h}, et D_{6h}



Cubique: T, T_h et T_d

	T	T_h	T_d
Objet			
Proj. stéréo.			
Exemple		B_{80}	 P_4O_{10}

Cubique: O et O_h

	O	O_h
Objet		
Proj. stéréo.		
Exemple		 SF_6

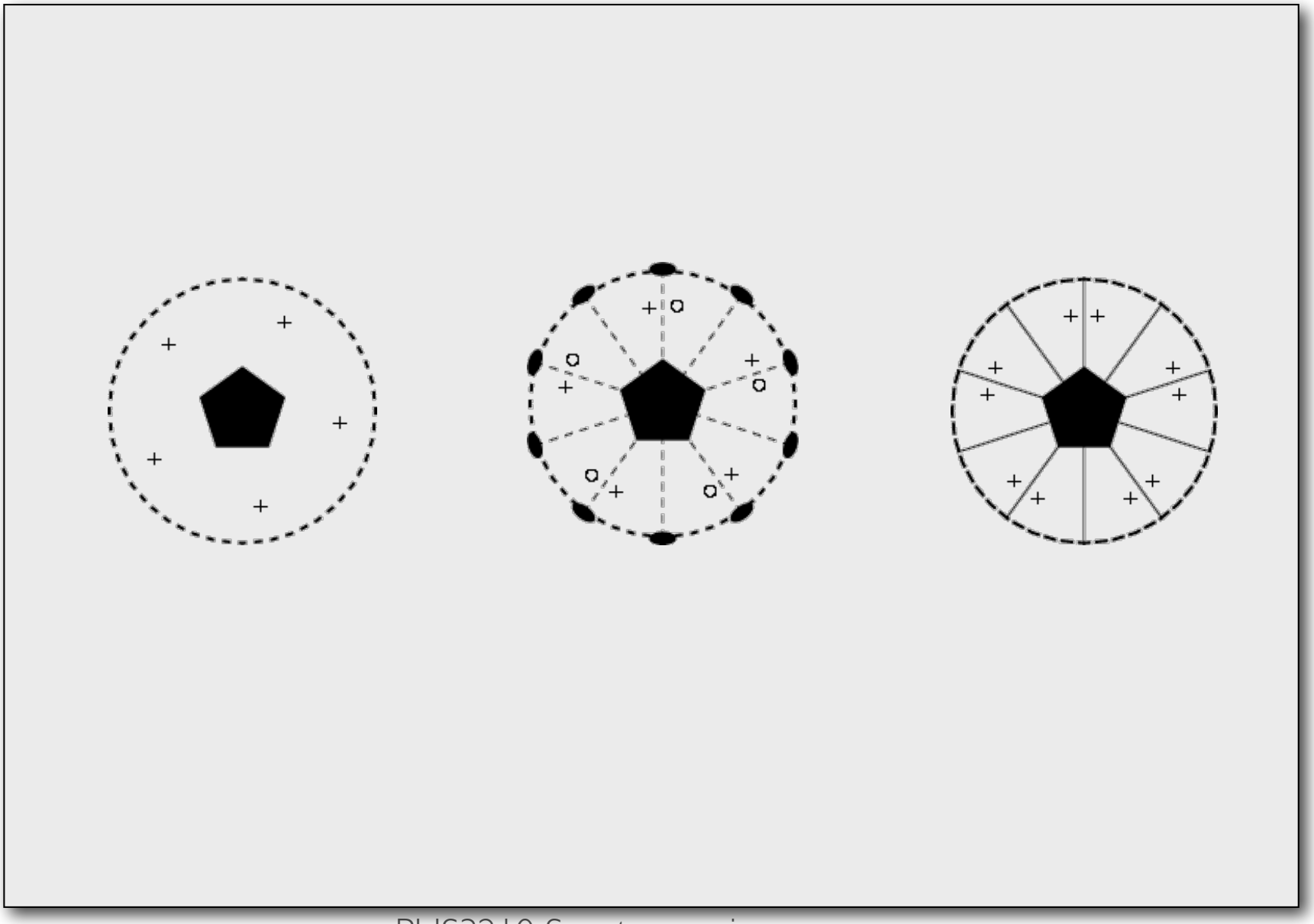
Non cristallographique: C_5, D_5 et C_{5v}

C_5 D_5 C_{5v}

Objet

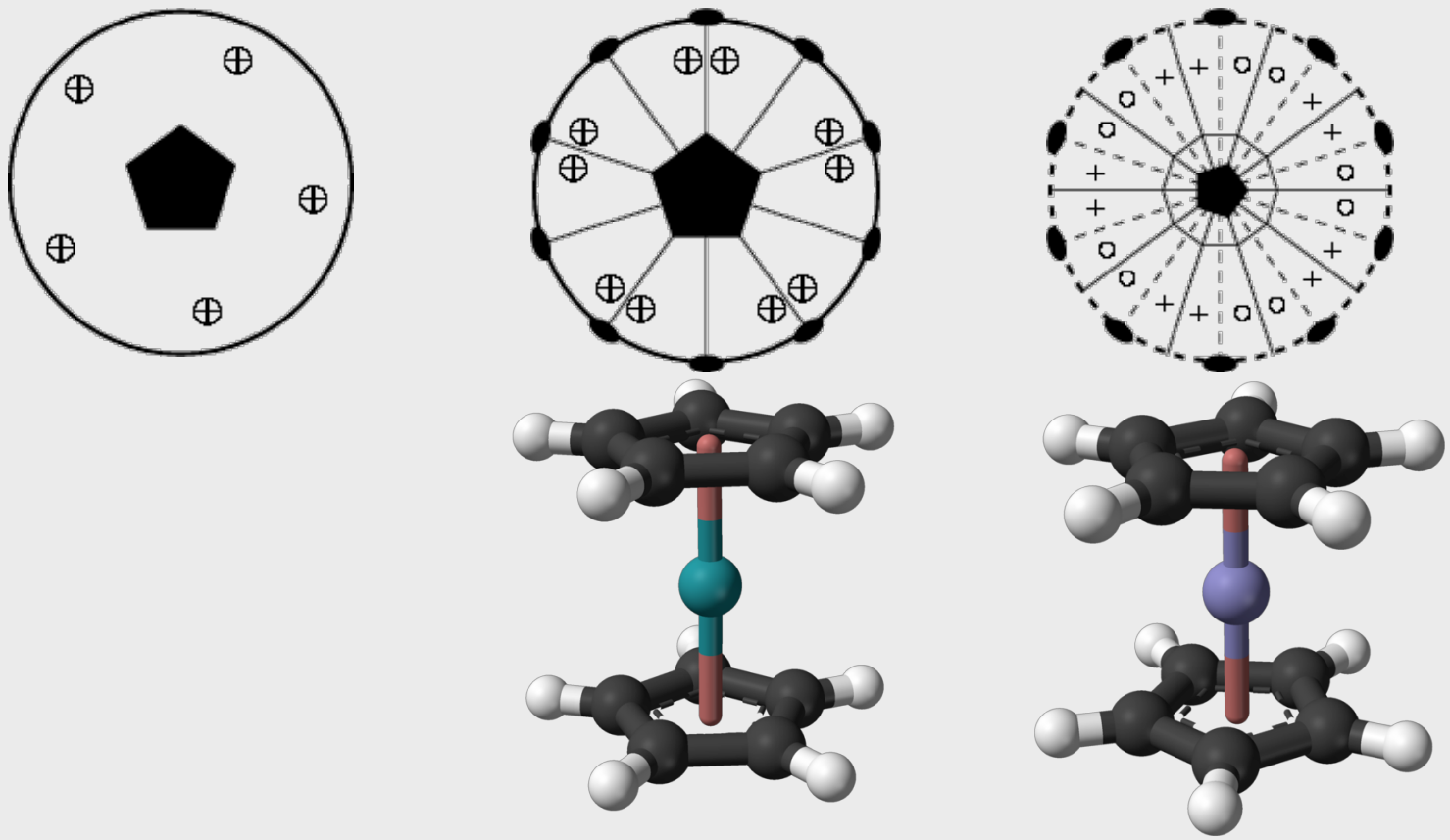
Proj. stéréo.

Exemple

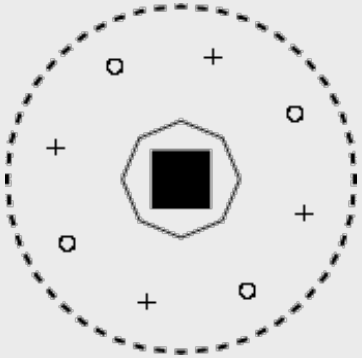
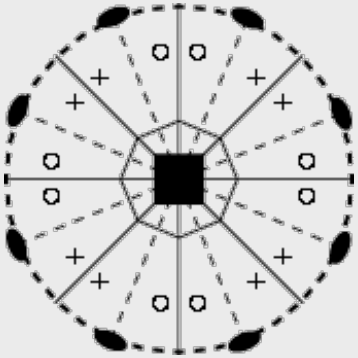
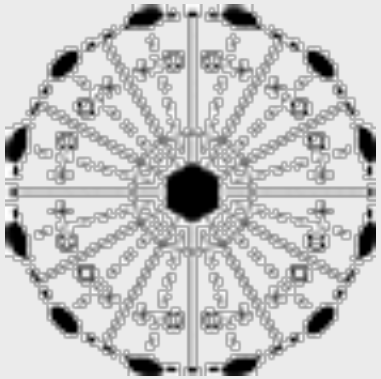
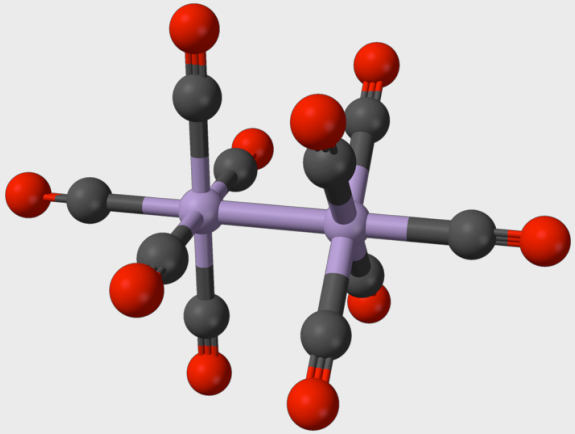
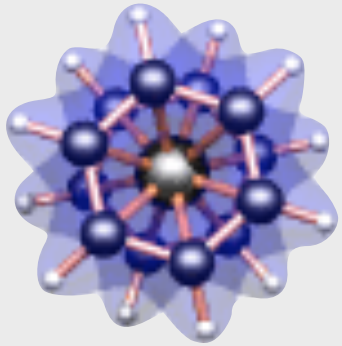


Non cristallographique: C_{5h}, D_{5d} et D_{5h}

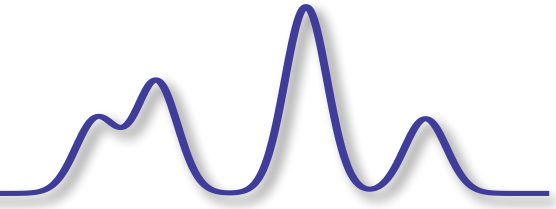
	C_{5h}	D_{5h}	D_{5d}
Objet			
Proj. stéréo.			
Exemple		$(C_5H_5)_2Ru$	$Fe(C_5H_5)_2$

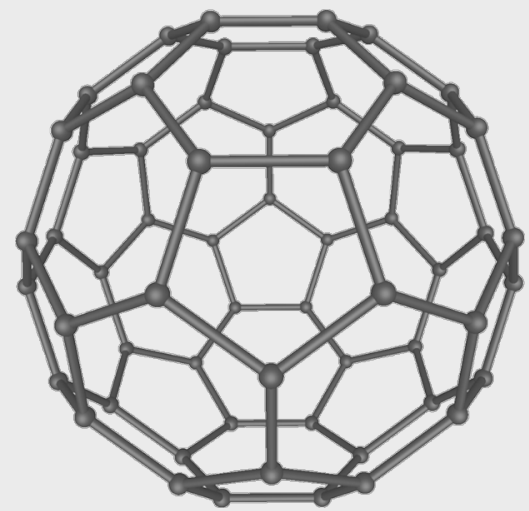


Non cristallographique: S_8, D_{4d} et D_{6d}

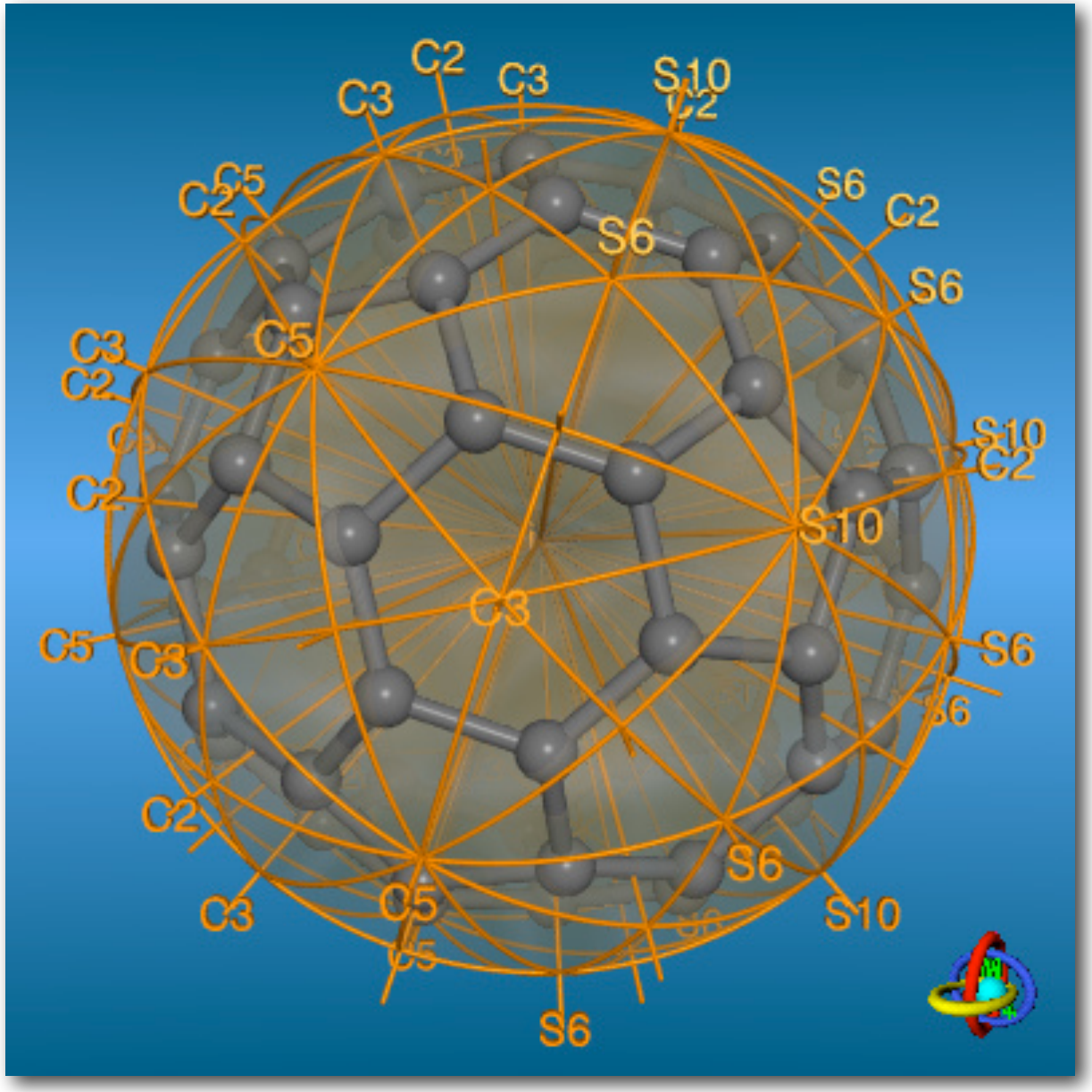
	S_8	D_{4d}	D_{6d}
Objet			
Proj. stéréo.			
Exemple		 $Mn_2(CO)_{10}$	 $Cr(C_6H_6)_2$

Non cristallographique: I et I_h



	I	I_h
Objet		
Proj. stéréo.		
Exemple		 C_{60}

I_h : 120 opérations de symétrie



Non crist.: C_∞, $C_{\infty h}$, $C_{\infty v}$ et $D_{\infty h}$

	C_∞	$C_{\infty h}$	$C_{\infty v}$	$D_{\infty v}$
Objet				
Proj. stéréo.				
Exemple			C_2O	CO_2

Les 32 groupes ponctuels (cryst.)

Famille	Schoenflies	Ordre	Internationale	Opérations
Cubique	O_h	48	m3m	E, $8C_3$, $6C_2$, $6C_4$, $3C_2'$, I, $6S_4$, $8S_6$, $3\sigma_h$, $6\sigma_d$
	T_d	24	$\bar{4}$3m	E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$
	O	24	432	E, $6C_4$, $8C_3$, $3C_2$, $6C_2'$
	T_h	24	m3	E, $8C_3$, $3C_2$, $3\sigma_v$, I, $8S_6$
	T	12	23	E, $4C_3$, $4C_3^2$, $3C_2$
Tétragonale	D_{4h}	16	4/mmm	E, $2C_4$, C_2, $2C_2'$, $2C_2''$, I, $2S_4$, σ_h, $2\sigma_v$, $2\sigma_d$
	D_{2d}	8	$\bar{4}$2m	E, $2S_4$, C_2, $2C_2'$, $2\sigma_d$
	C_{4v}	8	4mm	E, $2C_4$, C_2, $2\sigma_v$, $2\sigma_d$
	D_4	8	422	E, $2C_4$, C_2, $2C_2'$, $2C_2''$
	C_{4h}	8	4/m	E, C_4, C_2, C_4^3, i, S_4^3, σ_h, S_4
	S_4	4	$\bar{4}$	E, S_4, C_2, S_4^3
	C_4	4	4	E, C_4, C_2, C_4^3
Orthorhombique	D_{2h}	8	222	E, C_2, C_2', C_2'', i, σ, σ', σ''
	C_{2v}	4	mm2	E, C_2, σ_v' σ_v''
	D_2	4	mmm	E, C_2, C_2', C_2''

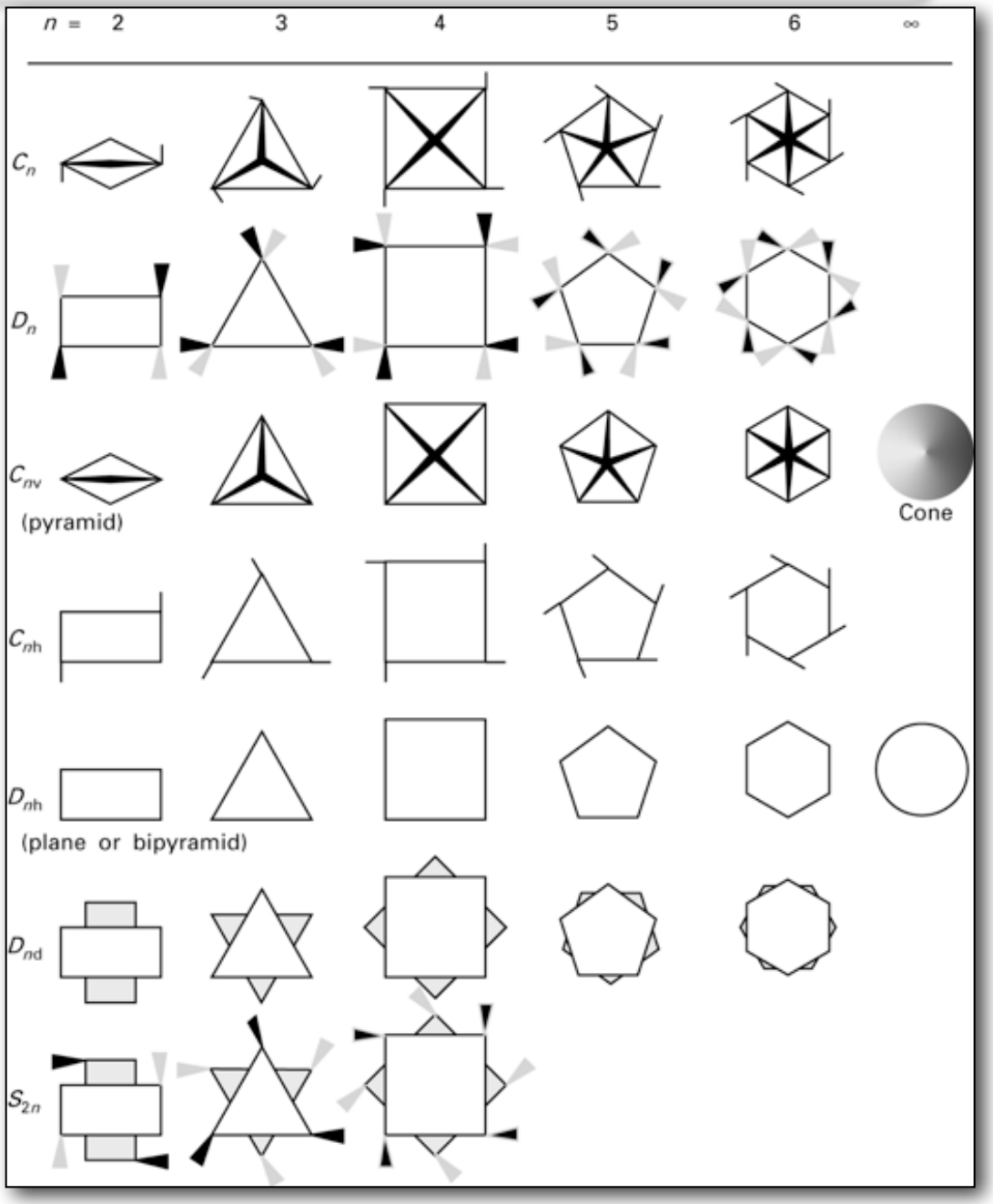
Les 32 groupes ponctuels (cryst.)

Famille	Schoenflies	Ordre	Internationale	Opérations
Hexagonale	D_{6h}	24	6/mmm	E, $2C_6$, $2C_3$, C_2, $3C_2'$, $3C_2''$, I, $2S_3$, $2S_6$, σ_h, $3\sigma_d$, $3\sigma_v$
	D_{3h}	12	$\bar{6}$m2	E, $2C_3$, $3C_2$, σ_h, $2S_3$, $3\sigma_v$
	C_{6v}	12	6mm	E, $2C_6$, $2C_3$, C_2, $3\sigma_v$, $3\sigma_d$
	D_6	12	622	E, $2C_6$, $2C_3$, C_2, $3C_2'$, $3C_2''$
	C_{6h}	12	6/m	E, C_6, C_3, C_2, C_3^2, C_6^5, i, S_3^2, S_6^5, σ_h, S_6, S_3
	C_{3h}	6	$\bar{6}$	E, C_3, C_3^2, σ_h, S_3, S_3^2
	C_6	6	6	E, C_6, C_3, C_2, C_3^2, C_6^5
Trigonale	D_{3d}	12	$\bar{3}$m	E, $2C_3$, $3C_2$, i, $2S_6$, $3\sigma_d$
	C_{3v}	6	3m	E, $2C_3$, $3\sigma_v$
	D_3	6	32	E, $2C_3$, $3C_2$
	S_6 ou C_{3i}	6	$\bar{3}$	E, C_3, C_3^2, i, S_6^5, S_6
	C_3	3	3	E, C_3, C_3^2
Monoclinique	C_{2h}	4	2/m	E, C_2, i, σ_h
	C_2	2	2	E, C_2
	C_s ou C_{1h}	2	m	E, σ_h
Triclinique	S_2 ou C_i	2	$\bar{1}$	E, I
	C_1	1	1	E

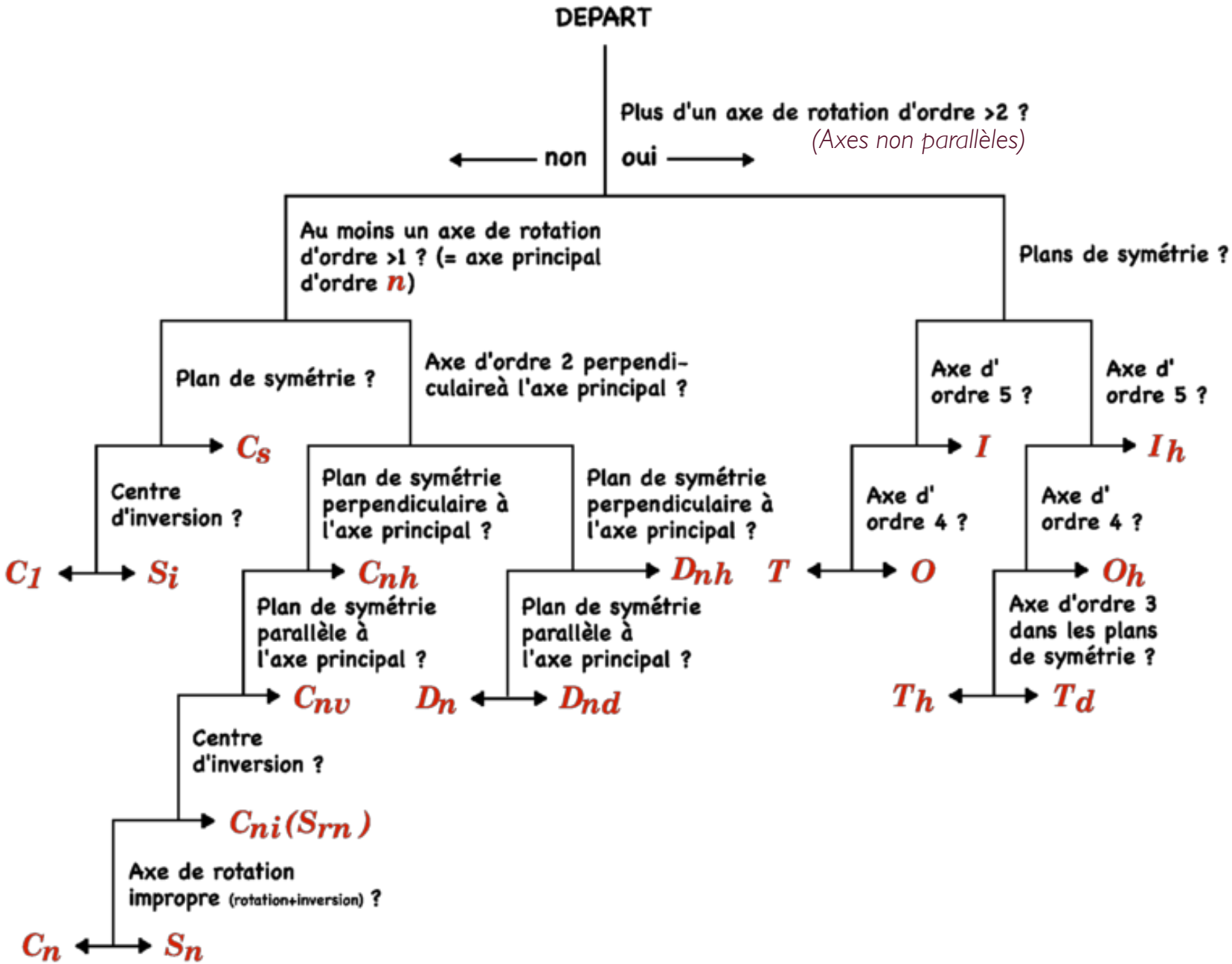
Les groupes ponctuels (non-cryst.)

Famille	Schoenflies	Ordre	Internationale	Opérations
Non cristallographique	I_h	120		E, $12C_5$, $12C_5^2$, $20C_3$, $15C_2$, i, $12S_{10}$, $12S_{10}^3$, $20S_6$, 15σ
	I	60		E, $12C_5$, $12C_5^2$, $20C_3$, $15C_2$
	D_{6d}	24		E, $2S_{12}$, $2C_6$, $2S_4$, $2C_3$, $2S_{12}^5$, C_2, $6C_2'$, $6\sigma_d$
	D_{5h}	20		E, $2C_5$, $2C_5^2$, $5C_2$, σ_h, $2S_5$, $2S_5^2$, $5\sigma_d$
	D_{5d}	20		E, $2C_5$, $2C_5^2$, $5C_2$, i, $2S_{10}$, $2S_{10}^3$, $5\sigma_d$
	D_{4d}	16		E, $2S_8$, $2C_4$, $2S_8^3$, C_2, $4C_2'$, $4\sigma_d$
	C_{5h}	10		E, C_5, C_5^2, C_5^3, C_5^4, σ_h, S_5, S_5^7, S_5^3, S_5^9
	C_{5v}	10		E, $2C_5$, $2C_5^2$, $5\sigma_v$
	D_5	10		E, $2C_5$, $2C_5^2$, $5C_2$
	S_8	8		E, S_8, C_4, S_8^3, C_2, S_8^5, C_4^3, S_8^7
	C_5	5	5	E, C_5, C_5^2, C_5^3, C_5^4
	$D_{\infty h}$	∞	∞/mm	E, $2C_{\infty\varphi}$, $\infty\sigma_v$, i, $2S_{\infty}\varphi$, ∞C_2
	$C_{\infty v}$	∞	∞/m	E, $2C_{\infty\varphi}$, $\infty\sigma v$
	$C_{\infty h}$	∞	∞/m	E, $2C_{\infty}\varphi$, i, $2S_{\infty}\varphi$
	C_{∞}	∞	∞	E, $2C_{\infty}\varphi$

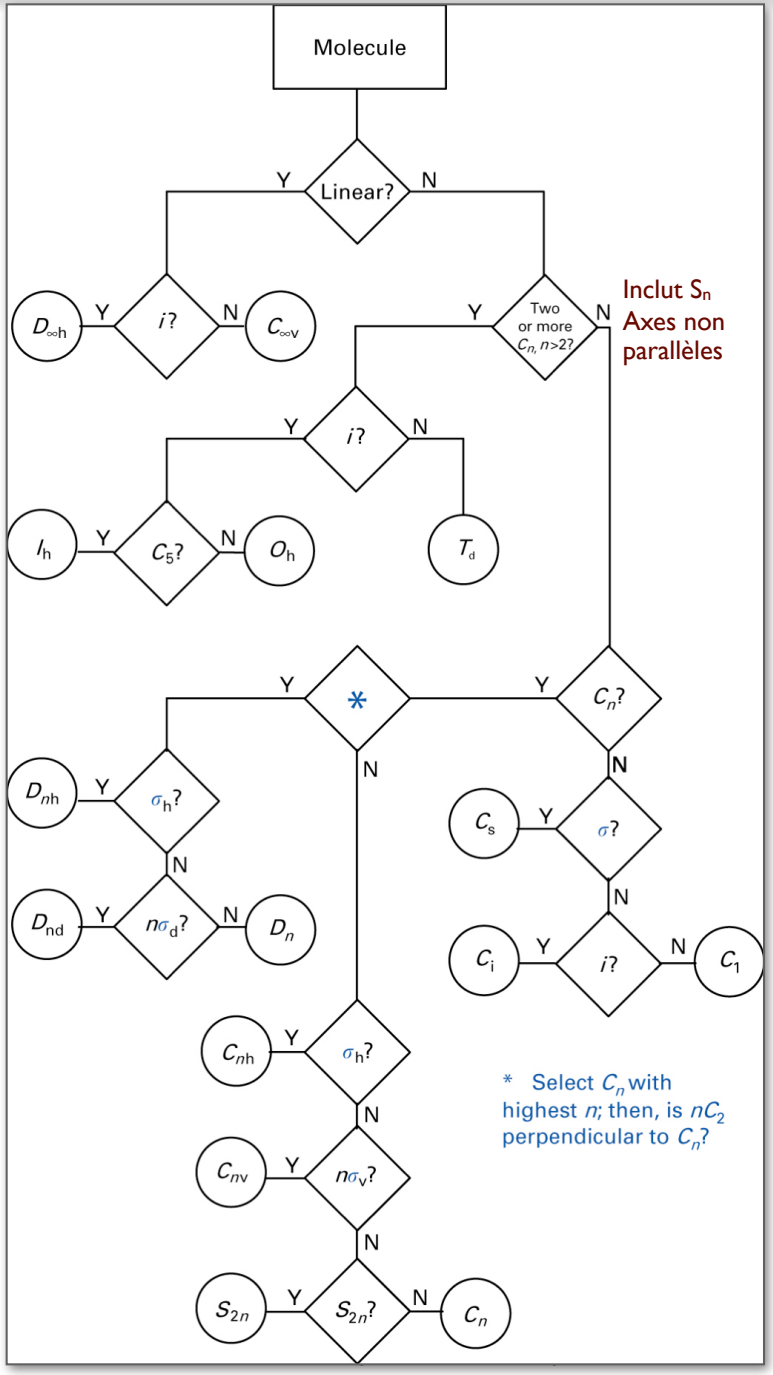
Exemples


n = 2
3
4
5
6
∞
C_n
D_n
C_{nv}
(pyramid)
Cone
C_{nh}
D_{nh}
(plane or bipyramid)
D_{nd}
S_{2n}

10. Détermination du groupe ponctuel



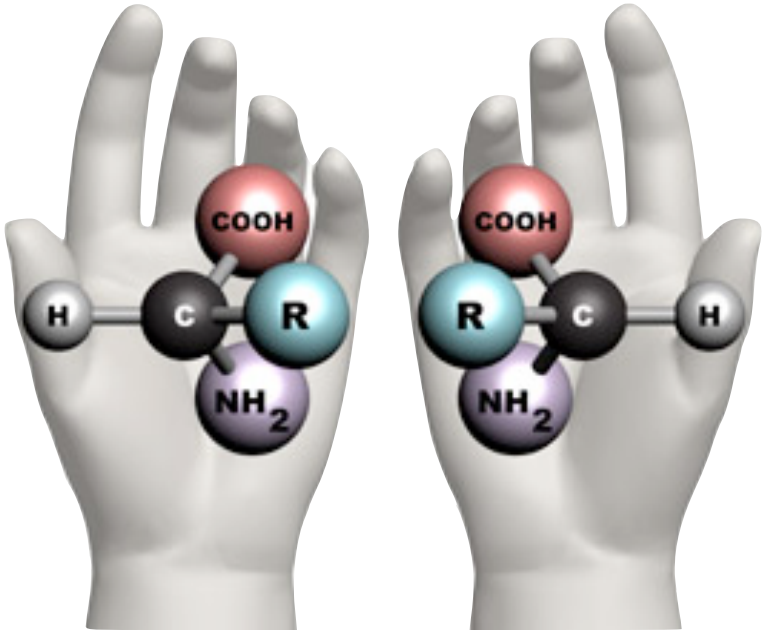
Détermination du groupe ponctuel



11. Chilarité

Définition 1

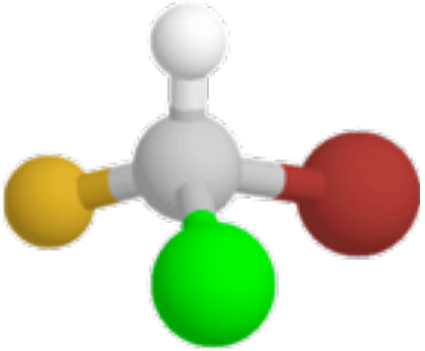
Une molécule est dite chirale si sa réflexion n'est pas identique à elle même.



Chilarité

Définition II

Une molécule est dite chirale si elle ne possède pas de rotoreflexion S_n (σ , I, S_3, S_4, ...)



Une molécule chirale

- Existe sous deux formes appelées énantiomères
- Les énantiomères présentent un pouvoir rotatoire (activité optique)
- L'énantiomère *d* et *l* tourne la polarisation de la lumière dans le sens antihoraire et horaire.
- Un mélange racémique (concentration égale des deux énantiomères) perd son pouvoir rotatoire.
- Les deux énantiomères ont parfois des propriétés chimiques remarquablement différentes.

Space groups

Definition
Symmorphic and non-symmorphic
From space groups to point groups

Les groupes d'espace sont essentiels pour l'étude des propriétés des matériaux cristallins. Malheureusement, nous n'aurons pas le temps ici de couvrir ce sujet.

Invariance of the Hamiltonian

Definition The symmetry operations characterizing the invariance of an Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})$$

form a space group. This group is composed of three types of operations,

Pure translations $$\boldsymbol{T} = n_a\boldsymbol{a} + n_b\boldsymbol{b} + n_c\boldsymbol{c}$$ *a, b, and c are the primitive translation vector*

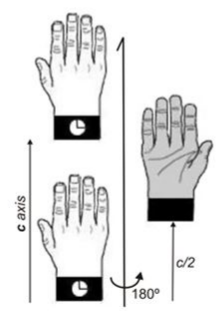
Pure rotations

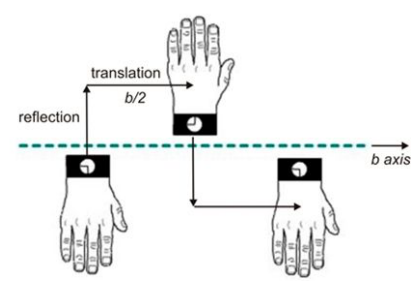
- E
- C_2, C_3, C_4, ... C_n
- I
- σ
- S_n (n>2)

Composite operations

Screw axis: Rotation followed by a fractional translation along the rotation axis

Glide plane: Mirror plane followed by a fractional translation along a direction in that plane





Space groups

Space groups

Crystal family	Crystal system	Required symmetries of point group	point groups	space groups	bravais lattices	Lattice system
Triclinic		None	2	2	1	Triclinic
Monoclinic		1 twofold axis of rotation or 1 mirror plane	3	13	2	Monoclinic
Orthorhombic		3 twofold axes of rotation or 1 twofold axis of rotation and two mirror planes.	3	59	4	Orthorhombic
Tetragonal		1 fourfold axis of rotation	7	68	2	Tetragonal
Hexagonal	Trigonal	1 threefold axis of rotation	5	7	1	Rhombohedral
				18	1	Hexagonal
	Hexagonal	1 sixfold axis of rotation	7	27		
Cubic		4 threefold axes of rotation	5	36	3	Cubic
Total: 6	7		32	230	14	7

From space groups to point groups

Space group symmetry operations (Seitz notation)

Lattice translation *Pure translation*

$$\{S|T_G\} = \{S|T + \tau_S\} = \{E|T\}\{S|\tau_S\}$$

Rotation *General translation* *Fractional translation* *Pure rotation if τ_s=0 Composite operation if not*

Symmorphic groups: with a proper choice of origin, τ_S=0 for all S

- The 74 symmorphic space groups are obtained by combination of the 32 crystallographic point groups and the the 14 Bravais lattice. Rotations and translation form two **independent** subgroups of the space group.
- Here, translations can be "factored out" by considering the crystal like a giant molecule and **the point group theory is sufficient to describe the physics occurring in the crystal.**

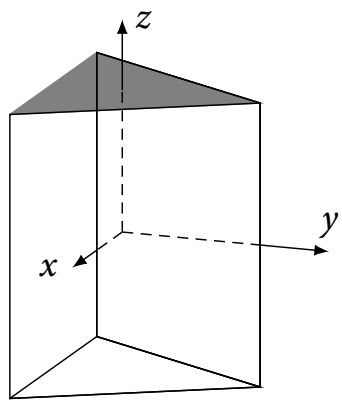
Non-symmorphic groups: $\tau_S \neq 0$ for some S

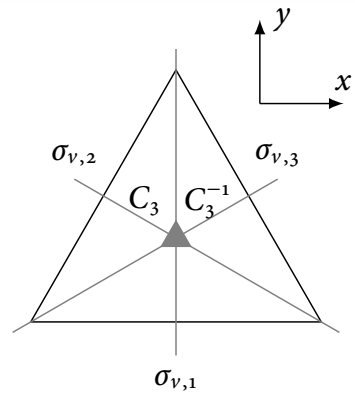
- The remaining 156 space groups are generated by replacing rotations with screw axes and mirror planes by glide planes in the 74 symmorphic groups.
- The point group cannot directly be used as above. However, with a suitable choice of origin, rotations and composite operations can be shown to form a group (factor group) which is **isomorphic to a crystallographic point group**.
- We can still use point group tables, but we have to remember to consider the effect of the fractional translation on wavefunctions.

Point group theory

Character table and irreducible representations
Representation theory
Great orthogonality theorem

The character table of C_{3v}





Symmetry operations grouped in classes

Group

$\{C_3, C_3^{-1}\}$

$\{\sigma_{v1}, \sigma_{v2}, \sigma_{v3}\}$

Irreps

$\mathbf{C}_{3v}$	E	$2C_3$	$3\sigma_v$	0	1	2
A_1	1	1	1	$\square 1$	$\square z$	$x^2+y^2, \square z^2$
A_2	1	1	-1		R_z	
E	2	-1	0		$\square(x,y),(R_x,R_y)$	$\square(xy, x^2-y^2), \square(zx, yz)$

Characters

Elementary functions transforming like these irreps

Irreducible representations (irreps)

Definition

Basis through which all the properties and phenomena can be decomposed (electronic states, vibrational states, ...).

Irreducible?

An infinite number of representations exists, irreducible representations provide the most convenient and simple basis to work with.

How many irreducible representations?

The number of irreducible representations equals the number of classes.

Example

The group C_{3v} has 3 classes and three representations.

$\mathbf{C}_{3v}$	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

** no spin yet*

Representation theory

For our purpose, group elements are symmetry operations leaving a Hamiltonian invariant.

These spatial transformations can naturally be ***represented*** by matrices.

For the group $$\mathcal{G} = \{g_1, g_2, g_3, \dots\}$$

we can build a representation

Square matrix of dimension l

$$\boldsymbol{D} = \{\boldsymbol{D}(g_1), \boldsymbol{D}(g_2), \boldsymbol{D}(g_3), \dots\}$$

The **faithful** representation ***D*** is composed of *h* square matrices of dimension *l* **isomorphic** with the group elements. That is,

if $g_i g_j = g_k$ then $\boldsymbol{D}(g_i)\boldsymbol{D}(g_j) = \boldsymbol{D}(g_k)$

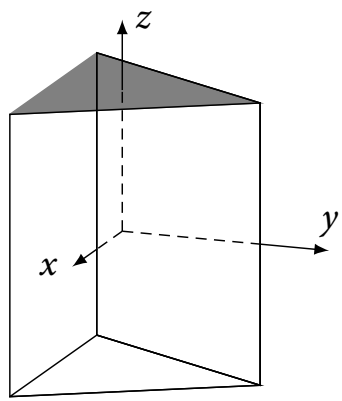
Identity matrix of dimension l

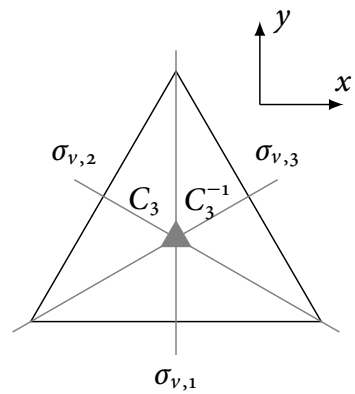
The condition EE=E reveal that $\boldsymbol{D}(E) = \mathbf{1}$

and it can be shown that $\boldsymbol{D}(g_1^{-1}) = \boldsymbol{D}(g_1)^{-1}$

There exists an infinite number of representations whose dimension can vary from 1 to infinity

A first representation for C_{3v}





We can generate a representation by expressing the effect of these transformations on a position vector (*l*=*3*): (x,y,z)

$$\boldsymbol{D}(E) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_{v,1}) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

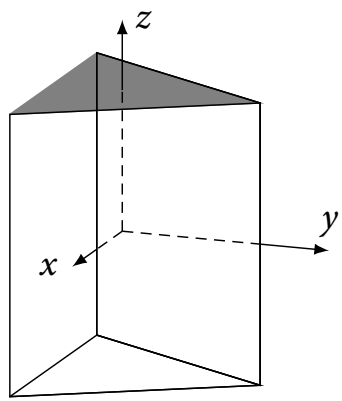
$$\boldsymbol{D}(C_3) = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_{v,2}) = \begin{bmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

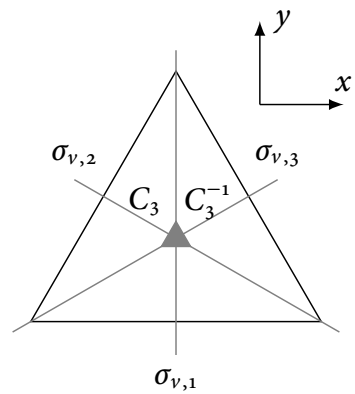
$$\boldsymbol{D}(C_3^{-1}) = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_{v,3}) = \begin{bmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

$\mathcal{C}_{3v\,(1\rightarrow,\,2\downarrow)}$	$\boldsymbol{D}(E)$	$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(\sigma_{v,2})$	$\boldsymbol{D}(\sigma_{v,3})$
$\boldsymbol{D}(E)$	$\boldsymbol{D}(E)$	$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(\sigma_{v,2})$	$\boldsymbol{D}(\sigma_{v,3})$
$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(E)$	$\boldsymbol{D}(\sigma_{v,2})$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(\sigma_{v,1})$
$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(E)$	$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(\sigma_{v,3})$
$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(E)$	$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(C_3)$
$\boldsymbol{D}(\sigma_{v,2})$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(E)$	$\boldsymbol{D}(C_3^{-1})$
$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(\sigma_{v,2})$	$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(E)$

$D^{(x,y,z)}$ is isomorphic with the group elements G

A second representation for C_{3v}





We can generate a different representation using a different object. Using a pseudovector (*l*=*3*): ***l*= *r* x *p*** = (l_x, l_y, l_z)

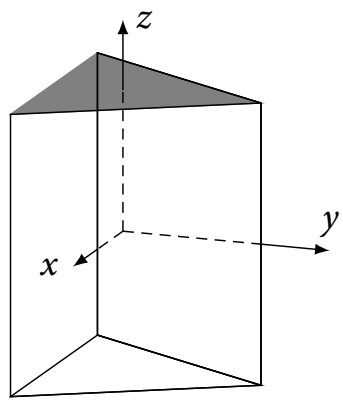
$$\boldsymbol{D}^{(l_x,l_y,l_z)}(E) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}^{(l_x,l_y,l_z)}(\sigma_{v,1}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix},$$

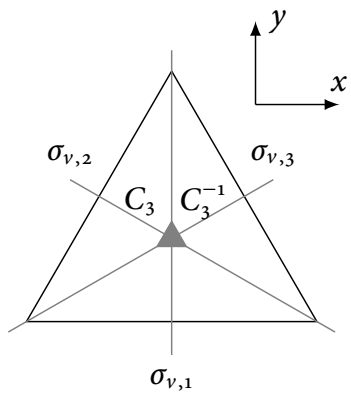
$$\boldsymbol{D}^{(l_x,l_y,l_z)}(C_3) = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}^{(l_x,l_y,l_z)}(\sigma_{v,2}) = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & -1 \end{bmatrix},$$

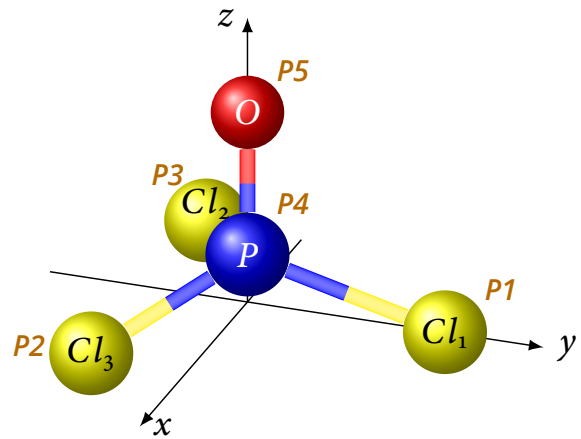
$$\boldsymbol{D}^{(l_x,l_y,l_z)}(C_3^{-1}) = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}^{(l_x,l_y,l_z)}(\sigma_{v,3}) = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & -1 \end{bmatrix}.$$

$D^{(lx,ly,lz)}$ is also isomorphic with the group elements G, yet it is different from $D^{(x,y,z)}$.

Yet another representation for C_{3v}







We can generate representations in an infinite number of ways.

Basis

$$\boldsymbol{V} = \begin{bmatrix} \text{Atom in P1} \\ \text{Atom in P2} \\ \text{Atom in P3} \\ \text{Atom in P4} \\ \text{Atom in P5} \end{bmatrix}$$

$$\boldsymbol{D}^{(\boldsymbol{V})}(E) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad \boldsymbol{D}^{(\boldsymbol{V})}(\sigma_{v,1}) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix},$$

$$\boldsymbol{D}^{(\boldsymbol{V})}(C_3) = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad \boldsymbol{D}^{(\boldsymbol{V})}(\sigma_{v,2}) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix},$$

$$\boldsymbol{D}^{(\boldsymbol{V})}(C_3^{-1}) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad \boldsymbol{D}^{(\boldsymbol{V})}(\sigma_{v,3}) = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

This representation is also isomorphic with the group elements G!

Towards irreducible representations

There exists an infinite number of possible representations. We want to find out the most convenient representations.

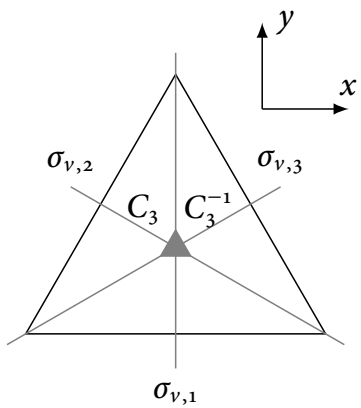
Equivalent representations

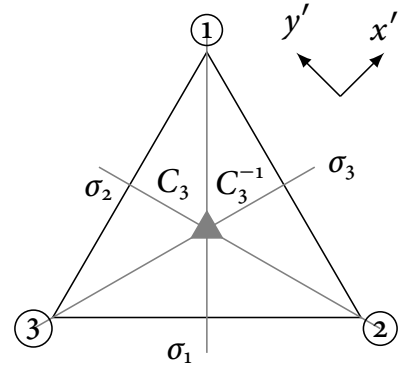
- Two faithful representations of group G, D and D', are equivalent if there exists an isometry S such that,

$$\boldsymbol{D}' = \{\boldsymbol{S}^{-1}\boldsymbol{D}(g_1)\boldsymbol{S}, \boldsymbol{S}^{-1}\boldsymbol{D}(g_2)\boldsymbol{S}, \boldsymbol{S}^{-1}\boldsymbol{D}(g_3)\boldsymbol{S}, \ldots\},$$

If no such isometry exists, then these representations are inequivalent.

Two equivalent representations





$$\boldsymbol{D}(E) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_{v,1}) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$\boldsymbol{D}(C_3) = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_{v,2}) = \begin{bmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$\boldsymbol{D}(C_3^{-1}) = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_{v,3}) = \begin{bmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

$$\boldsymbol{D}^{(x',y',z')}(E) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}^{(x',y',z')}(\sigma_1) = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$\boldsymbol{D}^{(x',y',z')}(C_3) = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}^{(x',y',z')}(\sigma_2) = \begin{bmatrix} -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\boldsymbol{D}^{(x',y',z')}(C_3^{-1}) = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \boldsymbol{D}^{(x',y',z')}(\sigma_3) = \begin{bmatrix} \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

These two representations are related to the following isometry,

$$\boldsymbol{S} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Towards irreducible representations

"Sum" of representations

Two representations, D' of dimension l' and D" of dimension l", can be added together to form a new representation D of dimension l'+l",

$$
\begin{aligned}
\boldsymbol{D} &= \boldsymbol{D}' \oplus \boldsymbol{D}'' \\
&= \{\boldsymbol{D}'(g_1) \oplus \boldsymbol{D}''(g_1), \boldsymbol{D}'(g_2) \oplus \boldsymbol{D}''(g_2), \ldots\} \\
&= \left\{ \begin{bmatrix} \boldsymbol{D}'(g_1) & \mathbf{0} \\ \mathbf{0} & \boldsymbol{D}''(g_1) \end{bmatrix}, \begin{bmatrix} \boldsymbol{D}'(g_2) & \mathbf{0} \\ \mathbf{0} & \boldsymbol{D}''(g_2) \end{bmatrix}, \ldots \right\}
\end{aligned}
$$

Null matrix

Note the Block diagonal form!

Reducible representations

A representation D is reducible if there exists an isometry such that D can be expressed as a sum of two representations

In other words, a representation D is reducible if there exists an isometry such that D can be brought into a block-diagonal form.

Irreducible representations

A representation is irreducible if it is of dimension 1, or if it there is not isometry allowing to express it with a block-diagonal form.

Is $D^{(x,y,z)}$ reducible ?

$$\boldsymbol{D}(E) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_{v,1}) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$\boldsymbol{D}(C_3) = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_{v,2}) = \begin{bmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$\boldsymbol{D}(C_3^{-1}) = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_{v,3}) = \begin{bmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Is $D^{(x,y,z)}$ reducible ? Yes

Yes, since it is block-diagonal

$$\boldsymbol{D}(E) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_{v,1}) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$\boldsymbol{D}(C_3) = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_{v,2}) = \begin{bmatrix} 1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$\boldsymbol{D}(C_3^{-1}) = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_{v,3}) = \begin{bmatrix} 1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

We have $\boldsymbol{D}^{(x,y,z)} = \boldsymbol{D}^{(x,y)} \oplus \boldsymbol{D}^{(z)}$

$$\boldsymbol{D}^{(z)} = \{[1], [1], [1], [1], [1], [1]\}$$ *Irreducible*

$$\boldsymbol{D}^{(x,y)} = \left\{ \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \tfrac{1}{2}\begin{bmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{bmatrix}, \tfrac{1}{2}\begin{bmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{bmatrix}, \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}, \tfrac{1}{2}\begin{bmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & -1 \end{bmatrix}, \tfrac{1}{2}\begin{bmatrix} 1 & \sqrt{3} \\ \sqrt{3} & -1 \end{bmatrix} \right\}$$

Is this reducible?

Is D(x,y) reducible ? Yes

$\mathcal{C}_{3v(1\rightarrow,2\downarrow)}$	$\boldsymbol{D}(E)$	$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(\sigma_{v,2})$	$\boldsymbol{D}(\sigma_{v,3})$
$\boldsymbol{D}(E)$	$\boldsymbol{D}(E)$	$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(\sigma_{v,2})$	$\boldsymbol{D}(\sigma_{v,3})$
$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(E)$	$\boldsymbol{D}(\sigma_{v,2})$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(\sigma_{v,1})$
$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(E)$	$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(\sigma_{v,3})$
$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(E)$	$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(C_3)$
$\boldsymbol{D}(\sigma_{v,2})$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(E)$	$\boldsymbol{D}(C_3^{-1})$
$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(\sigma_{v,3})$	$\boldsymbol{D}(\sigma_{v,2})$	$\boldsymbol{D}(\sigma_{v,1})$	$\boldsymbol{D}(C_3^{-1})$	$\boldsymbol{D}(C_3)$	$\boldsymbol{D}(E)$

Is there an isometry such that all the matrices of this representation,

$$\boldsymbol{D}^{(x,y)} = \left\{ \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \frac{1}{2}\begin{bmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{bmatrix}, \frac{1}{2}\begin{bmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{bmatrix}, \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}, \frac{1}{2}\begin{bmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & -1 \end{bmatrix}, \frac{1}{2}\begin{bmatrix} 1 & \sqrt{3} \\ \sqrt{3} & -1 \end{bmatrix} \right\}$$

can be simultaneously diagonalized?

For 2D representation, the task is simplified by the fact that block diagonal 2D matrices commute. Therefore, we need to find out if there exists an isometry

$$\boldsymbol{S} = \begin{bmatrix} a & b \\ c & d \end{bmatrix}$$

that generates a representation **D'** such [**D'**(g_i), **D'**(g_j)]=0.

$$\begin{aligned}
&\left[\boldsymbol{D}'^{(x,y)}(g_i), \boldsymbol{D}'^{(x,y)}(g_j)\right] \\
&= \left(\boldsymbol{S}^{-1}\boldsymbol{D}^{(x,y)}(g_i)\boldsymbol{S}\right)\left(\boldsymbol{S}^{-1}\boldsymbol{D}^{(x,y)}(g_j)\boldsymbol{S}\right) - \left(\boldsymbol{S}^{-1}\boldsymbol{D}^{(x,y)}(g_j)\boldsymbol{S}\right)\left(\boldsymbol{S}^{-1}\boldsymbol{D}^{(x,y)}(g_i)\boldsymbol{S}\right) \\
&= \boldsymbol{S}^{-1}\boldsymbol{D}^{(x,y)}(g_i)\boldsymbol{D}^{(x,y)}(g_j)\boldsymbol{S} - \boldsymbol{S}^{-1}\boldsymbol{D}^{(x,y)}(g_j)\boldsymbol{D}^{(x,y)}(g_i)\boldsymbol{S}
\end{aligned}$$

Multiplying on the left by S and on the right by S^{-1}

$$= \boldsymbol{D}^{(x,y)}(g_i)\boldsymbol{D}^{(x,y)}(g_j) - \boldsymbol{D}^{(x,y)}(g_j)\boldsymbol{D}^{(x,y)}(g_i)$$

This is equal to zero only if operations, g_i and g_j commute. This is not the case here and this representation is irreducible.

What can be said about abelian point groups?

Is $D^{(lx,ly,lz)}$ reducible ? Yes

$$\boldsymbol{D}^{(l_x,l_y,l_z)}(E) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}^{(l_x,l_y,l_z)}(\sigma_{v,1}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix},$$

$$\boldsymbol{D}^{(l_x,l_y,l_z)}(C_3) = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}^{(l_x,l_y,l_z)}(\sigma_{v,2}) = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & -1 \end{bmatrix},$$

$$\boldsymbol{D}^{(l_x,l_y,l_z)}(C_3^{-1}) = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}^{(l_x,l_y,l_z)}(\sigma_{v,3}) = \begin{bmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & -1 \end{bmatrix}.$$

We have $$\boldsymbol{D}^{(l_x,l_y,l_z)} = \boldsymbol{D}^{(l_x,l_y)} \oplus \boldsymbol{D}^{(l_z)}$$

$$\boldsymbol{D}^{(l_z)} = \{[1],[1],[1],[-1],[-1],[-1]\}$$ *Irreducible and new*

$$\boldsymbol{D}^{(l_x,l_y)} = \boldsymbol{D}^{(x,y)}$$ *Two equivalent representations*

Reducible ?

Is this representation of C3v reducible?

$$\boldsymbol{D}(E) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_1) = \begin{bmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{bmatrix},$$

$$\boldsymbol{D}(C_3) = \frac{1}{2}\begin{bmatrix} 0 & -\sqrt{\frac{3}{2}} & -1 \\ \sqrt{\frac{3}{2}} & -1 & \sqrt{\frac{3}{2}} \\ -1 & -\sqrt{\frac{3}{2}} & 0 \end{bmatrix}, \qquad \boldsymbol{D}(C_3^{-1}) = \frac{1}{2}\begin{bmatrix} 0 & \sqrt{\frac{3}{2}} & -1 \\ -\sqrt{\frac{3}{2}} & -1 & -\sqrt{\frac{3}{2}} \\ -1 & \sqrt{\frac{3}{2}} & 0 \end{bmatrix}$$

$$\boldsymbol{D}(\sigma_2) = \frac{1}{2}\begin{bmatrix} 1 & -\sqrt{\frac{3}{2}} & 0 \\ -\sqrt{\frac{3}{2}} & -1 & -\sqrt{\frac{3}{2}} \\ 0 & -\sqrt{\frac{3}{2}} & 1 \end{bmatrix}, \qquad \boldsymbol{D}(\sigma_3) = \frac{1}{2}\begin{bmatrix} 1 & \sqrt{\frac{3}{2}} & 0 \\ \sqrt{\frac{3}{2}} & -1 & \sqrt{\frac{3}{2}} \\ 0 & \sqrt{\frac{3}{2}} & 1 \end{bmatrix},$$

It is not diagonal, but the following isometry transforms this representation into a black diagonal form,

$$\boldsymbol{S} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{bmatrix},$$

This isometry corresponds to a π/4 rotation around y.

This particular representation is equivalent to $D^{(x,y,z)}$

C3v irreducible representations

By playing around, we have found the 3 irreducible representations of C_{3v}.

$$\boldsymbol{D}^{(z)} = \{[1],[1],[1],[1],[1],[1]\}$$

$$\boldsymbol{D}^{(l_z)} = \{[1],[1],[1],[-1],[-1],[-1]\}$$

$$\boldsymbol{D}^{(x,y)} = \left\{\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}, \frac{1}{2}\begin{bmatrix}-1 & -\sqrt{3}\\\sqrt{3} & -1\end{bmatrix}, \frac{1}{2}\begin{bmatrix}-1 & \sqrt{3}\\-\sqrt{3} & -1\end{bmatrix}, \begin{bmatrix}-1 & 0\\0 & 1\end{bmatrix}, \frac{1}{2}\begin{bmatrix}1 & -\sqrt{3}\\-\sqrt{3} & -1\end{bmatrix}, \frac{1}{2}\begin{bmatrix}1 & \sqrt{3}\\\sqrt{3} & -1\end{bmatrix}\right\}$$

C3v character table

Let's organize these representations in the form of a table.

C_{3v}	E	C_3	C_3^{-1}	σ_{v1}	σ_{v2}	σ_{v3}
$D^{(z)}$	$\begin{bmatrix}1\end{bmatrix}$	$\begin{bmatrix}1\end{bmatrix}$	$\begin{bmatrix}1\end{bmatrix}$	$\begin{bmatrix}1\end{bmatrix}$	$\begin{bmatrix}1\end{bmatrix}$	$\begin{bmatrix}1\end{bmatrix}$
$D^{(l_z)}$	$\begin{bmatrix}1\end{bmatrix}$	$\begin{bmatrix}1\end{bmatrix}$	$\begin{bmatrix}1\end{bmatrix}$	$\begin{bmatrix}-1\end{bmatrix}$	$\begin{bmatrix}-1\end{bmatrix}$	$\begin{bmatrix}-1\end{bmatrix}$
$D^{(x,y)}$	$\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}$	$\frac{1}{2}\begin{bmatrix}-1 & -\sqrt{3}\\ \sqrt{3} & -1\end{bmatrix}$	$\frac{1}{2}\begin{bmatrix}-1 & \sqrt{3}\\ -\sqrt{3} & -1\end{bmatrix}$	$\begin{bmatrix}-1 & 0\\ 0 & 1\end{bmatrix}$	$\frac{1}{2}\begin{bmatrix}1 & -\sqrt{3}\\ -\sqrt{3} & -1\end{bmatrix}$	$\frac{1}{2}\begin{bmatrix}1 & \sqrt{3}\\ \sqrt{3} & -1\end{bmatrix}$

Les caractères

Définition

Le caractère d'une représentation ***D(g$_i$)*** est simplement la trace de la matrice

$$\underbrace{\chi(g_i)}_{\textit{Caractère}} = \sum_l D_{ll}(g_i) = \underbrace{\mathrm{tr}}_{\textit{Trace}} D(g_i)$$

Deux représentations semblables, ***D*** et ***D'***, c'est-à-dire deux transformations reliées entre elles par un changement de base, possède le même caractère.

Ainsi, on utilisera le caractère plutôt que la matrice elle-même afuib de s'affranchir des particularités de la base choisie pour déterminer les irreps.

C3v character table

Let's organize these representations in the form of a table.

C_{3v}	E	C_3	C_3^{-1}	σ_{v1}	σ_{v2}	σ_{v3}
$D^{(z)}$	$[1]$	$[1]$	$[1]$	$[1]$	$[1]$	$[1]$
$D^{(l_z)}$	$[1]$	$[1]$	$[1]$	$[-1]$	$[-1]$	$[-1]$
$D^{(x,y)}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\frac{1}{2}\begin{bmatrix} -1 & -\sqrt{3} \\ \sqrt{3} & -1 \end{bmatrix}$	$\frac{1}{2}\begin{bmatrix} -1 & \sqrt{3} \\ -\sqrt{3} & -1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$	$\frac{1}{2}\begin{bmatrix} 1 & -\sqrt{3} \\ -\sqrt{3} & -1 \end{bmatrix}$	$\frac{1}{2}\begin{bmatrix} 1 & \sqrt{3} \\ \sqrt{3} & -1 \end{bmatrix}$

It can be shown (using the GOT) that all equivalent representations have the same character (or trace).

C_{3v}	E	C_3	C_3^{-1}	σ_{v1}	σ_{v2}	σ_{v3}
$D^{(z)}$	1	1	1	1	1	1
$D^{(l_z)}$	1	1	1	-1	-1	-1
$D^{(x,y)}$	2	-1	-1	0	0	0

Furthermore, conjugate operations always share the same character.

C_{3v}	E	$2C_3$	$3\sigma_v$
$D^{(z)}$	1	1	1
$D^{(l_z)}$	1	1	-1
$D^{(x,y)}$	2	-1	0

C3v character table

Mulliken's notation (*not always respected)

R. S. Mulliken, J. Chem. Phys., 1955, 23, 1997; 1956, 24, 1118)

Symbol	Property
A	1D representation. Symmetric with respect to rotation around the principal rotational axis
B	1D representation. Anti-symmetric with respect to rotation around the principal rotational axis
E	2D representation ("entartet")
T	3D representation
subscript 1	symmetric with respect to a C_2 (1st choice) or vertical mirror plane (2nd choice) perpendicular to the principal axis.
subscript 2	anti-symmetric with respect to C_2 (1st choice) or a vertical mirror plane (2nd choice) perpendicular to the principal axis.
subscript g	symmetric with respect to a center of symmetry ("gerade")
subscript u	anti-symmetric with respect to a center of symmetry ("ungerade)
prime (')	symmetric with respect to a mirror plane parallel to the principal rotational axis
double prime (")	anti-symmetric with respect to a mirror plane parallel to the principal rotational axis

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	l_z
E	2	-1	0	$(x, y), (l_x, l_y)$

Let's take a shorter and foolproof approach

D_{3h}	E	$2C_3$	$3C'_2$ $3C'_2$	σ_h σ_h	$2S_3$	$3\sigma_v$ $3\sigma_v$	-E	$2\text{-}C_3$	$2\text{-}S_3$
A'_1	1	1	1	1	1	1	1	1	1
A'_2	1	1	-1	1	1	-1	1	1	1
E'	2	-1	0	2	-1	0	2	-1	-1
A''_1	1	1	1	-1	-1	-1	1	1	-1
A''_2	1	1	-1	-1	-1	1	1	1	-1
E''	2	-1	0	-2	1	0	2	-1	1
$E_{1/2}$	2	1	0	0	$\sqrt{3}$	0	-2	-1	$-\sqrt{3}$
$E_{5/2}$	2	1	0	0	$-\sqrt{3}$	0	-2	-1	$\sqrt{3}$
$E_{3/2}$	2	-2	0	0	0	0	-2	2	0

Great orthogonality theorem

Irrep α

Order of the group

$$\sum_i D^{(\alpha)}_{pq}(g_i)\left(D^{(\alpha')}_{p'q'}(g_i)\right)^* = \frac{h}{l_\alpha}\delta_{\alpha,\alpha'}\delta_{p,p'}\delta_{q,q'}$$

Sum of group elements

Matrix element

Dimension of irrep α

Great orthogonality theorem

The approach we have used to build the character table of C_{3v} works, but it becomes tedious to find the irreps of larger point groups. We will instead use the sophisticated tools of group theory.

From these properties and lemma,

1) Representations are composed of unitary matrices
2) Shur's first lemma (irreducible representations)

   A representation **D** is irreducible if the the only matrix simultaneous commuting with all the matrices forming D takes the form **M**=c**1.**

3) Shur's second lemma (two non-equivalent irreducible representations)

   Assuming two irreducible representations $\mathbf{D}^{(1)}$ and $\mathbf{D}^{(2)}$ of dimension l_1 and l_2 and the following relation,

$$\boldsymbol{M}\boldsymbol{D}^{(1)}(g_i) = \boldsymbol{D}^{(2)}(g_i)\boldsymbol{M} \quad \forall g_i \in \mathcal{G}.$$

   - If l_1 is different than l_2, then **M=0**
   - If l_1=l_2, the representation are irreducible if **M=0.** Otherwise, they are equivalent.

we can derive the great orthogonality theorem.

Great orthogonality theorem

Two unitary irreducible representations, $D^{(\alpha)}$ and $D^{(\alpha')}$ always satisfy the great orthogonality theorem.

Irrep α

Order of the group

$$\sum_i D^{(\alpha)}_{pq}(g_i)\left(D^{(\alpha')}_{p'q'}(g_i)\right)^* = \frac{h}{l_\alpha}\delta_{\alpha,\alpha'}\delta_{p,p'}\delta_{q,q'}$$

Sum over group elements

Matrix element

Dimension of irrep α

As we find it convenient to work with characters, the GOT can be used to derive two orthogonality relationships

First little theorem

Sum over classes

Character of irrep α and class i

$$\sum_{\mathcal{K}_i} n(\mathcal{K}_i)\chi^{(\alpha)}(\mathcal{K}_i)^*\chi^{(\alpha')}(\mathcal{K}_i) = h\delta_{\alpha\alpha'}$$

Number of elements in this class

Second little theorem

Sum over irreps

Order of the group

$$\sum_\alpha \chi^{(\alpha)}(\mathcal{K}_i)^*\chi^{(\alpha)}(\mathcal{K}_j) = \frac{h}{n(\mathcal{K}_i)}\delta_{\mathcal{K}_i,\mathcal{K}_j}$$

Character of irrep α and class i

Irreps and Classes behave like orthogonal vectors

First little theorem (orthogonal irreps)

$$\sum_{\mathcal{K}_i} n(\mathcal{K}_i)\chi^{(\alpha)}(\mathcal{K}_i)^*\chi^{(\alpha')}(\mathcal{K}_i) = h\delta_{\alpha\alpha'}$$

With $V_{\mathcal{K}_i}^{(\alpha)} = \sqrt{n(\mathcal{K}_i)}\chi^{(\alpha)}(\mathcal{K}_i)$

and $V_{\mathcal{K}_i}^{(\alpha')} = \sqrt{n(\mathcal{K}_i)}\chi^{(\alpha')}(\mathcal{K}_i)$

then

$$\sum_{\mathcal{K}_i} V_{\mathcal{K}_i}^{(\alpha)^*} V_{\mathcal{K}_i}^{(\alpha')} = \underbrace{\boldsymbol{V}^{(\alpha)^*} \cdot \boldsymbol{V}^{\alpha'}}_{\text{Scalar product}} = \underbrace{h\delta_{\alpha,\alpha'}}_{\text{Orthogonality}}$$

Second little theorem (orthogonal classes)

$$\sum_{\alpha} \chi^{(\alpha)}(\mathcal{K}_i)^*\chi^{(\alpha)}(\mathcal{K}_j) = \frac{h}{n(\mathcal{K}_i)}\delta_{\mathcal{K}_i,\mathcal{K}_j}$$

With $V_{\mathcal{K}_i}^{(\alpha)} = \chi^{(\alpha)}(\mathcal{K}_i)$

and $V_{\mathcal{K}_j}^{(\alpha)} = \chi^{(\alpha)}(\mathcal{K}_j)$

then

$$\sum_{\alpha} V_{\mathcal{K}_i}^{(\alpha)^*} V_{\mathcal{K}_j}^{(\alpha)} = \underbrace{\boldsymbol{V}_{\mathcal{K}_i}{}^* \cdot \boldsymbol{V}_{\mathcal{K}_j}}_{\text{Scalar product}} = \underbrace{\frac{h}{n(\mathcal{K}_i)}\delta_{\mathcal{K}_i,\mathcal{K}_j}}_{\text{Orthogonality}}$$

Graphical representation of theorems

Second little theorem:
orthogonality between columns

$$\sum_{\alpha} \chi^{(\alpha)}(\mathcal{K}_i)^* \chi^{(\alpha)}(\mathcal{K}_j) = \frac{h}{n(\mathcal{K}_i)} \delta_{\mathcal{K}_i,\mathcal{K}_j}$$

First little theorem:
orthogonality between rows

$$\sum_{\mathcal{K}_i} n(\mathcal{K}_i) \chi^{(\alpha)}(\mathcal{K}_i)^* \chi^{(\alpha')}(\mathcal{K}_i) = h\delta_{\alpha\alpha'}$$

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

How to calculate character tables

1) The number of irreps equals the number of classes.

2) All groups include a 1D totally symmetric irrep (A_1, A'_1, A_g, Γ_1).

3) The character $X^{(\alpha)}(E)$ is always a positive integer (real and non-zero).

4) The product of classes can always be expressed as a sum of classes

$$\mathcal{K}_i \odot \mathcal{K}_j = \sum_k \boxed{c_k} \mathcal{K}_k \qquad n(\mathcal{K}_i)\chi^{(\alpha)}(\mathcal{K}_i)\; n(\mathcal{K}_j)\chi^{(\alpha)}(\mathcal{K}_j) = d_\alpha \sum_k \boxed{c_k} n(\mathcal{K}_k)\chi^{(\alpha)}(\mathcal{K}_k)$$

5) The second little theorem
Always apply on class E first

$$\sum_\alpha \chi^{(\alpha)}(\mathcal{K}_i)^* \chi^{(\alpha)}(\mathcal{K}_j) = \frac{h}{n(\mathcal{K}_i)} \delta_{\mathcal{K}_i,\mathcal{K}_j}$$

6) The first little theorem

$$\sum_{\mathcal{K}_i} n(\mathcal{K}_i)\chi^{(\alpha)}(\mathcal{K}_i)^* \chi^{(\alpha')}(\mathcal{K}_i) = h\delta_{\alpha\alpha'}$$

La table des caractères du groupe C_{3v}

Éléments de symétrie: $E,\ C_3,\ C_3^{-1},\ \sigma_{v1},\ \sigma_{v2},\ \sigma_{v3}$

Ordre du groupe: $h = 6$

Nombre de classes: 3

1) On ajoute la représentation infidèle.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
l_2	a	c	e
l_3	b	d	f

2) Le 2e PT appliqué sur la classe E donne

$$1 + |a|^2 + |b|^2 = 6$$

Puisque a et b sont les dimensions des irreps, ils doivent nécessairement être réels. Ces dimensions sont 1 et 2.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
l_2	1	c	e
l_3	2	d	f

La table des caractères du groupe C_{3v}

3) Appliquons le produit de classes sur la classe C_3. $\mathbb{C}_i \cdot \mathbb{C}_j = \sum_s c_s \mathbb{C}_s$

$$\left(\mathrm{C}_3 + \mathrm{C}_3^{-1}\right) \cdot \left(\mathrm{C}_3 + \mathrm{C}_3^{-1}\right) = \mathrm{C}_3^{-1} + \mathrm{E} + \mathrm{E} + \mathrm{C}_3$$
$$= 2\mathrm{E} + 1\left(\mathrm{C}_3 + \mathrm{C}_3^{-1}\right)$$

Continuons avec la relation

$$g(\mathbb{C}_i)\chi^{(l)}(\mathbb{C}_i)\; g(\mathbb{C}_j)\chi^{(l)}(\mathbb{C}_j) = d_l \sum_s c_s g(\mathbb{C}_s)\chi^{(l)}(\mathbb{C}_s)$$

appliquée à l'irrep l_2 $\quad 2c \cdot 2c = 1(2 \cdot 1 \cdot 1 + 1 \cdot 2 \cdot c)$

$$0 = 4c^2 - 2c - 2 \quad \Rightarrow \quad \begin{array}{l} c = 1 \\ c = -1/2 \end{array}$$

Attention: la solution est parfois un nombre complexe.

appliquée à l'irrep l_3 $\quad 2d \cdot 2d = 2(2 \cdot 1 \cdot 2 + 1 \cdot 2 \cdot d)$

$$0 = 4d^2 - 4d - 8$$

$$\Rightarrow \quad \begin{array}{l} d = -1 \\ d = 2 \end{array}$$

À l'aide du 1re PTO sur la classe C_3 on trouve aussi $1 + |c|^2 + |d|^2 = 6/2$, donc $c = 1 \quad d = -1$

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
l_2	1	1	e
l_3	2	-1	f

La table des caractères du groupe C_{3v}

4) Le 1er PTO sur A_1 et I_2 donne

$$1 \cdot 1 \cdot 1 + 2 \cdot 1 \cdot 1 + 3 \cdot 1 \cdot e = 0$$
$$\Rightarrow e = -1$$

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
I_2	1	1	e
I_3	2	-1	f

5) Le 1e PTO sur A_1 et I_3

$$1 \cdot 1 \cdot 2 + 2 \cdot 1 \cdot -1 + 3 \cdot 1 \cdot f = 0$$
$$\Rightarrow f = 0$$

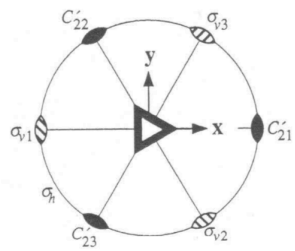
C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
I_2	1	1	-1
I_3	2	-1	f

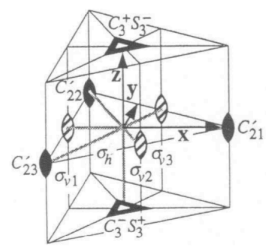
6) La notation de Mulliken

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

The D3h character table

$\boxed{\text{Group } D_{3h}}$





- Symmetry operations:

  $E, C_3, C_3^{-1}, C'_{21}, C'_{22}, C'_{23}, \sigma_h, S_3, S_3^{-1}, \sigma_{v1}, \sigma_{v2}, \sigma_{v3}$

- Order of the group: $h = 12$

- Number of classes:

  $\{E\}$ Always a single-element class (same for the inversion)

  $\{C_3, C_3^{-1}\}$ because of C'_2 or σ_v

  $\{C'_{21}, C'_{22}, C'_{23}\}$ because of C_3

  $\{\sigma_h\}$ Single element class (often the case, but not always)

  $\{S_3, S_3^{-1}\}$ because of C'_2 or σ_v

  $\{\sigma_{v1}, \sigma_{v2}, \sigma_{v3}\}$ because of C_3

  Number of classes $= 6$

  $\Rightarrow$ Number of irreps $= 6$

$$C_3 = C_{21} C_3^{-1} C_{21}$$
$$C_{21} = C_3^{-1} C_{22} C_3$$
$$C_{22} = C_3^{-1} C_{23} C_3$$
$$S_3 = \sigma_{v1} S_3^{-1} \sigma_{v1}$$
$$\sigma_{v1} = C_3^{-1} \sigma_{v2} S_3$$
$$\sigma_{v2} = S_3^{-1} \sigma_{v3} S_3$$

The D3h character table

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
α_1						
α_2						
α_3						
α_4						
α_5						
α_6						

We need to determine the $6 \times 6 = 36$ characters.

The D3h character table

- Let's add the totally symmetric representation

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
α_2	a					
α_3	b					
α_4	c					
α_5	d					
α_6	e					

- Let's apply the 2nd LOT on class E

$$\sum_{\alpha} \chi^{(\alpha)}(E)^* \chi^{(\alpha)}(E) = 1 + |a|^2 + |b|^2 + |c|^2 + |d|^2 + |e|^2 = 12$$

What is the solution?

The D3h character table

Let's use the fact that these five characters are positive integers : 1, 2, 3, ... Why?

Hence, the only solution is $1+1+1+1+2^2+2^2=12$.

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
α_2	1					
α_3	1					
α_4	1					
α_5	2					
α_6	2					

The D3h character table

- Lets multiply class $2C_3$ with itself.

$$\{C_3, C_3^{-1}\} \odot \{C_3, C_3^{-1}\} = C_3^{-1} \oplus E \oplus E \oplus C_3 = 2\{E\} \oplus \{C_3, C_3^{-1}\}$$

and use the decomposition relation

$$n(C_3)\, \chi^{(\alpha)}(C_3) \cdot n(C_3)\, \chi^{(\alpha)}(C_3) = d_\alpha \sum_k c_k\, n(K_k)\, \chi^{(\alpha)}(K_k)$$

For α_2, α_3 and α_4, $d_\alpha = 1$ and we get the equation

$$4\underbrace{\chi^{(\alpha)}(C_3)^2}_{x} = 1\left(2\cdot 1\, \underbrace{\chi^{(\alpha)}(E)}_{=1} + 1\cdot 2\cdot \underbrace{\chi^{(\alpha)}(C_3)}_{x}\right)$$

$$4x^2 = 2 + 2x \Rightarrow \boxed{x = 1} \text{ or } x = -1/2$$

why?

For α_5 and α_6, $d_\alpha = 2$ and we get the equation

$$4\underbrace{\chi^{(\alpha)}(C_3)^2}_{y} = 2\left(2\cdot 1\, \underbrace{\chi^{(\alpha)}(E)}_{2} + 1\cdot 2\cdot \underbrace{\chi^{(\alpha)}(C_3)}_{y}\right)$$

$$4y^2 = 8 + 4y \Rightarrow y = -1 \text{ or } y = 2$$

The D3h character table

To determine the correct solution we can apply the 2 LOT on class C_3

$$\sum_{\alpha} \chi^{(\alpha)}(C_3)^* \chi^{(\alpha)}(C_3) = \frac{12}{2} = 6$$

$$1 + 1 + 1 + 1 + y_1^2 + y_2^2 = 6$$

The only acceptable solution is then that both characters are equal to -1

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
α_2	1	1				
α_3	1	1				
α_4	1	1				
α_5	2	-1				
α_6	2	-1				

The D3h character table

- Let's multiply class σ_n with itself.

$$\{\sigma_n\} \odot \{\sigma_n\} = 1\,\{E\}$$ and the decomposition relation

$$n(\sigma_n)\,\chi^{(\alpha)}(\sigma_n)\,n(\sigma_n)\,\chi^{(\alpha)}(\sigma_n) = d_\alpha\left[1\,\underbrace{n(E)}_{1}\,\chi^{(\alpha)}(E)\right]$$

$$\chi^{(\alpha)}(\sigma_n)^2 = d_\alpha\,\chi^{(\alpha)}(E)$$

For irreps with $d_\alpha = 1$, $\chi^{(\alpha)}(E) = 1$ and then $\chi^{(\alpha)}(\sigma_n) = \pm 1$

For irreps with $d_\alpha = 2$, $\chi^{(\alpha)}(E) = 2$ and then $\chi^{(\alpha)}(\sigma_n) = \pm 2$

D_{3h}	E	$2C_3$	$3C_2'$	σ_n	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
α_2	1	1		1 or -1		
α_3	1	1		1 or -1		
α_4	1	1		1 or -1		
α_5	2	-1		2 or -2		
α_6	2	-1		2 or -2		

The D3h character table

Let's now apply the 2LOT on E and σ_h

$$\sum_\alpha \chi^\alpha(E)^* \chi^\alpha(\sigma_h) = 0$$

Then solution is

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
α_2	1	1	$e^{i\theta_a}$	1		
α_3	1	1	$e^{i\theta_b}$	-1		
α_4	1	1	$e^{i\theta_c}$	-1		
α_5	2	-1	$de^{i\theta_d}$	2		
α_6	2	-1	$fe^{i\theta_f}$	-2		

where d and f are real.

- 2nd LOT on C_2'

$$1+1+1+1+d^2+f^2 = \frac{12}{3} = 4$$

$$d^2+f^2=0 \Rightarrow \boxed{d=f=0}$$

- 2nd LOT on C_2' and E and C_2' and σ_h

$$1+e^{i\theta_a}+e^{i\theta_b}+e^{i\theta_c} = 0$$

$$1+e^{i\theta_a}-e^{i\theta_b}-e^{i\theta_c} = 0$$

$$\Rightarrow \boxed{e^{i\theta_a}=-1}, \quad e^{i\theta_b} = -e^{i\theta_c}$$

The D3h character table

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
α_2	1	1	$\boxed{-1}$	1		$\boxed{-1}$
α_3	1	1	$e^{i\theta_b}$	-1	$e^{i\theta_k}$	$e^{i\theta_k}$
α_4	1	1	$-e^{i\theta_b}$	-1		$-e^{i\theta_k}$
α_5	2	-1	$\boxed{0}$	2		$\boxed{0}$
α_6	2	-1	$\boxed{0}$	-2		$\boxed{0}$

same equation, same solution

- 2nd LOT on C_2' and σ_v

$$1 + 1 + e^{i(\theta_b+\theta_k)} + e^{i(\theta_b+\theta_k)} = 0$$

$$2\cos(\theta_b+\theta_k) = -2 \Rightarrow \theta_b+\theta_k = \pi$$

(no need to account for other solutions)

- 1st LOT on A_1' and α_3

$$1 + 2 + 3e^{i\theta_b} - 1 + 2e^{i\theta_k} - 3e^{-i\theta_b} = 0$$

$$2 + \underbrace{3\cdot 2i\sin\theta_b}_{\text{purely imaginary.}} + 2e^{i\theta_k} = 0$$

$$\hookrightarrow 2 + 2\,\mathrm{Re}[e^{i\theta_k}] = 0 \Rightarrow \mathrm{Re}[e^{i\theta_k}] = -1 \Rightarrow \theta_k = \pi$$

then the imaginary part is $0 \Rightarrow \theta_b = 0$

The D3h character table

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
α_2	1	1	-1	1		-1
α_3	1	1	$\boxed{1}$	-1	$\boxed{-1}$	$\boxed{-1}$
α_4	1	1	$\boxed{-1}$	-1		$\boxed{1}$
α_5	2	-1	0	2		0
α_6	2	-1	0	-2		0

It is trivial to find the remaining characters,

Koster		D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
Γ_1		A_1'	1	1	1	1	1	1
Γ_2	A_2'	α_2	$\boxed{1}$	$\boxed{1}_A$	$\boxed{-1}_2$	$\boxed{1}'$	1	-1
Γ_3	A_1''	α_3	$\boxed{1}$	$\boxed{1}_A$	$\boxed{1}_1$	$\boxed{-1}''$	-1	-1
Γ_4	A_2''	α_4	$\boxed{1}$	$\boxed{1}_A$	$\boxed{-1}_2$	$\boxed{-1}''$	-1	1
Γ_5	E'	α_5	$\boxed{2}_E$	-1	0	$\boxed{2}'$	-1	0
Γ_6	E''	α_6	$\boxed{2}_E$	-1	0	$\boxed{-2}''$	1	0

Mulliken notation not fully respected

The D3h character table

$\mathbf{D}_{3h}$	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	−1	1	1	−1
E'	2	−1	0	2	−1	0
A_1''	1	1	1	−1	−1	−1
A_2''	1	1	−1	−1	−1	1
E''	2	−1	0	−2	1	0

Looking carefully do you notice some symmetry in the structure of the table?

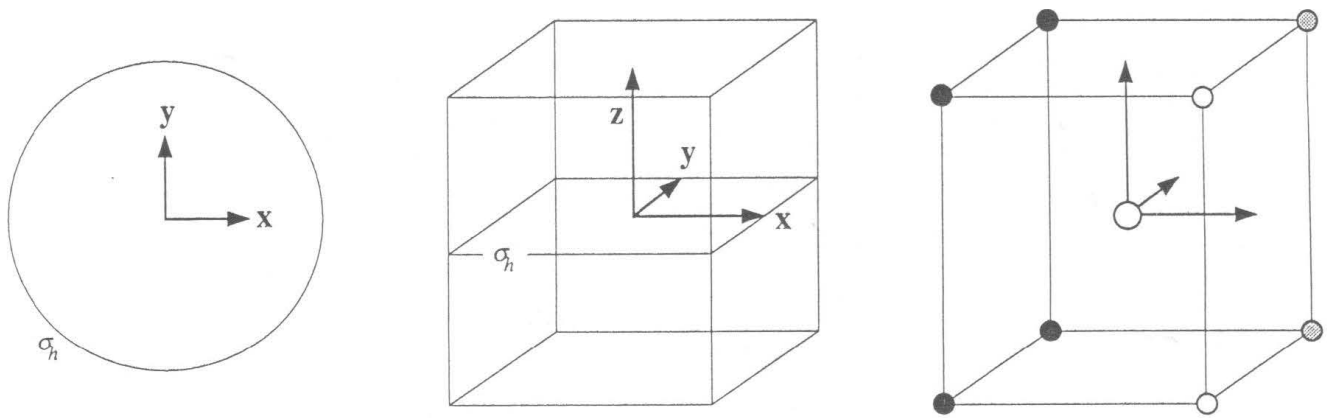
The D3h character table

$\mathbf{D}_{3h}$	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Point group C_s

Group C_s Two symmetry operations: E, σ_h

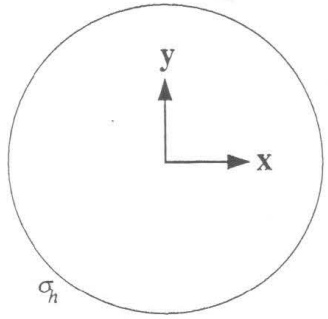


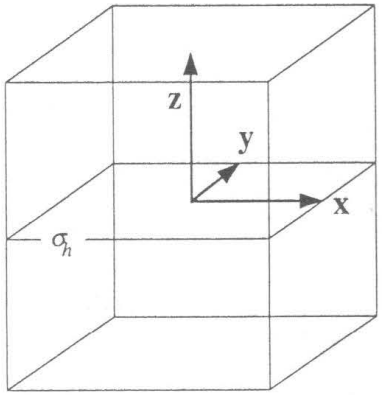
Example

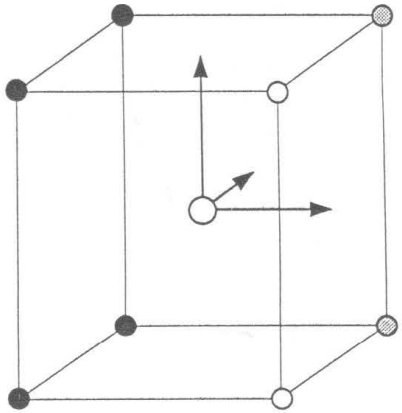
What is the character table?

Point group C_s

Group C_s Two symmetry operations: E, σ_h







Example

What is the character table?

C_s	E	σ_h
A'	1	1
A''	1	-1

The easier path to the D3h character table

$$\overbrace{\{E,\ C_3,\ C_3^{-1},\ \sigma_{v1},\ \sigma_{v2},\ \sigma_{v3}\}}^{C_{3v}} \cdot \overbrace{\{E,\ \sigma_h\}}^{C_{1h}=C_s} =$$

$$\overbrace{\{\underbrace{E,\ C_3,\ C_3^{-1},\sigma_{v1},\ \sigma_{v2},\ \sigma_{v3},}_{E\ x\ C_{3v}}\ \underbrace{\sigma_h,\ S_3,\ S_3^{-1},\ C_{21},\ C_{22},\ C_{23}}_{\sigma_h\ x\ C_{3v}}\}}^{D_{3h}}$$

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

x

C_s	E	σ_h
A'	1	1
A''	1	-1

=

D_{3h}	E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

Decomposition of reducible representations

An reducible representation can be expressed as the sum of irreducible representation

$$l_r = n^{(\alpha_1)} l^{(\alpha_1)} \oplus n^{(\alpha_2)} l^{(\alpha_2)} \oplus \cdots = \sum_{\alpha_i} n^{(\alpha_i)} l^{(\alpha_i)}$$

Reducible representation

Irrep.

Obviously, this relationship is also valid for characters

$$\chi_r(\mathcal{K}_j) = \sum_{\alpha_i} n^{(\alpha_i)} \chi^{(\alpha_i)}(\mathcal{K}_j)$$

Using orthogonality relationships, we find this incredibly useful relation

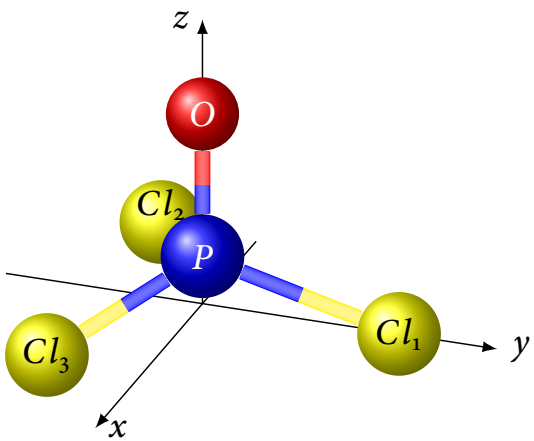
$$n^{(\alpha_i)} = \frac{1}{h} \sum_{\mathcal{K}_j} g(\mathcal{K}_j) \chi^{(\alpha_i)}(\mathcal{K}_j)^* \chi_r(\mathcal{K}_j)$$

C_{3v} example

$$\boldsymbol{D}^{(x,y,z)} = \boldsymbol{D}^{(x,y)} \oplus \boldsymbol{D}^{(z)}$$

$$\chi_r(E) = 1 \times 2 + 1 \times 1 = 3$$
$$\chi_r(2C_3) = 1 \times (-1) + 1 \times 1 = 0$$
$$\chi_r(3\sigma_v) = 1 \times 0 + 1 \times 1 = 1$$

Remember about this 5D representation of C_{3v}?



$$\boldsymbol{D}^{(V)}(E) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad \boldsymbol{D}^{(V)}(\sigma_{v,1}) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix},$$

$$\boldsymbol{D}^{(V)}(C_3) = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad \boldsymbol{D}^{(V)}(\sigma_{v,2}) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix},$$

$$\boldsymbol{D}^{(V)}(C_3^{-1}) = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \quad \boldsymbol{D}^{(V)}(\sigma_{v,3}) = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

Naturally, this representation is reducible since the maximum dimension is 2.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$D^{(V)}$	5	2	3

$$n^{(\alpha_i)} = \frac{1}{h} \sum_{\mathcal{K}_j} g(\mathcal{K}_j) \chi^{(\alpha_i)}(\mathcal{K}_j)^* \chi_r(\mathcal{K}_j)$$

$$n^{(A_1)} = \frac{1}{6}(1 \cdot 1 \cdot 5 + 2 \cdot 1 \cdot 2 + 3 \cdot 1 \cdot 3) = 3$$

$$n^{(A_2)} = \frac{1}{6}(1 \cdot 1 \cdot 5 + 2 \cdot 1 \cdot 2 + 3 \cdot (-1) \cdot 3) = 0$$

$$n^{(E)} = \frac{1}{6}(1 \cdot 2 \cdot 5 + 2 \cdot (-1) \cdot 2 + 3 \cdot 0 \cdot 3) = 1$$

$$\boxed{D^{(V)} = 3A_1 \oplus E}$$

Multiplication of representation

The product of two representations can be easily calculated using the irrep multiplication table.

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	L_z
E	2	-1	0	(x,y)
$A_1 \times A_1$	1	1	1	z^2
$A_1 \times A_2$	1	1	-1	$z\ l_z$
$A_1 \times E$	2	-1	0	(zx,zy)
$A_2 \times A_2$	1	1	1	L_z^2
$A_2 \times E$	2	-1	0	(L_zx,L_zy)
$E \times E$	4	1	0	(x^2, y^2, xy, yx)

What does the product of two 2D irreps mean?

It is the dyadic product of the representations

$$\boldsymbol{D}^{(x,y)} = \left\{ \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}, \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}, \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}, \begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}, \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \right\}$$

$$D^{(E)}(E) \otimes D^{(E)}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$\chi(E) = 4$

$$D^{E}(C_3) \otimes D^{(E)}(C_3) = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\frac{\sqrt{3}}{2} & -1/2 \end{pmatrix} \otimes \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\frac{\sqrt{3}}{2} & -1/2 \end{pmatrix}$$

$$= \frac{1}{4} \begin{pmatrix} 1 & -\sqrt{3} & -\sqrt{3} & 3 \\ \sqrt{3} & 1 & -3 & -\sqrt{3} \\ \sqrt{3} & -3 & 1 & -\sqrt{3} \\ 3 & \sqrt{3} & +\sqrt{3} & 1 \end{pmatrix}$$

$\chi(C_3) = 1$

$$D^{(E)}(\sigma_{v1}) \otimes D^{(E)}(\sigma_{v1}) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$\chi(\sigma_v) = 0$

Multiplication of representation

The product of two representations can be easily calculated using the irrep multiplication table.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$A_1 \times A_1$	1	1	1
$A_1 \times A_2$	1	1	-1
$A_1 \times E$	2	-1	0
$A_2 \times A_2$	1	1	1
$A_2 \times E$	2	-1	0
$E \times E$	4	1	0

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	?

Multiplication of representation

The product of two representations can be easily calculated using the irrep multiplication table.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$A_1 \times A_1$	1	1	1
$A_1 \times A_2$	1	1	-1
$A_1 \times E$	2	-1	0
$A_2 \times A_2$	1	1	1
$A_2 \times E$	2	-1	0
$E \times E$	4	1	0

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	A_1+A_2+E

Symmetrization of the ExE product

$(x,y) \otimes (p_x, p_y) = xp_x,\ xp_y,\ yp_x,\ yp_y$

We know that this product transforms as $A_1 \oplus A_2 \oplus E$

What is the linear combination transforming as A_1?

$$\boxed{xp_x + yp_y}$$

$$E(xp_x + yp_y) = 1(xp_x + yp_y) \qquad \chi(E) = 1$$

$$C_3(xp_x + yp_y) = \left(-\frac{x}{2} + \frac{\sqrt{3}}{2}y\right)\left(-\frac{p_x}{2} + \frac{\sqrt{3}}{2}p_y\right) + \left(-\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right)\left(-\frac{\sqrt{3}}{2}p_x - \frac{1}{2}p_y\right)$$

$$= \frac{xp_x}{4} - \frac{\sqrt{3}}{4}xp_y - \frac{\sqrt{3}}{4}yp_x + \frac{3}{4}yp_y + \frac{3}{4}xp_x + \frac{\sqrt{3}}{4}xp_y + \frac{\sqrt{3}}{4}yp_x + \frac{yp_y}{4}$$

$$= 1(xp_x + yp_y) \qquad \chi(C_3) = 1$$

$$\sigma_v(xp_x + yp_y) = 1(xp_x + yp_y) \qquad \chi(\sigma_v) = 1$$

It transforms as A_1

What is the linear combination transforming as A_2?

$$\boxed{xp_y - yp_x}$$

We have already demonstrated the transformation property of l_z

Symmetrization of the ExE product

What is the linear combination transforming as E?

$$\boxed{\left(xp_x - yp_y,\ xp_y + yp_x \right)}$$

$\chi(E) = 2$

$\chi(\sigma_v) = 0$

$$C_3\left(xp_x - yp_y,\ xp_y + yp_x\right)$$

$$= \left[\left(-\frac{x}{2} + \frac{\sqrt{3}}{2}y\right)\left(-\frac{p_x}{2} + \frac{\sqrt{3}}{2}p_y\right) - \left(-\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right)\left(-\frac{\sqrt{3}}{2}p_x - \frac{1}{2}p_y\right),\right.$$
$$\left.\left(-\frac{x}{2} + \frac{\sqrt{3}}{2}y\right)\left(-\frac{\sqrt{3}}{2}p_x - \frac{1}{2}p_y\right) + \left(-\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right)\left(-\frac{p_x}{2} + \frac{\sqrt{3}}{2}p_y\right)\right]$$

$$= \left[\left(\frac{xp_x}{4} - \frac{\sqrt{3}}{4}xp_y - \frac{\sqrt{3}}{4}yp_x + \frac{3}{4}yp_y - \frac{3}{4}xp_x - \frac{\sqrt{3}}{4}xp_y - \frac{\sqrt{3}}{4}yp_x - \frac{yp_y}{4}\right)\right.$$
$$\left.,\left(\frac{\sqrt{3}}{4}xp_x + \frac{xp_y}{4} - \frac{3}{4}yp_x - \frac{\sqrt{3}}{4}yp_y + \frac{\sqrt{3}}{4}xp_x - \frac{3}{4}xp_y + \frac{yp_x}{4} - \frac{\sqrt{3}}{4}yp_y\right)\right]$$

$$= \left[-\frac{1}{2}xp_x + \frac{1}{2}yp_y - \frac{\sqrt{3}}{2}xp_y - \frac{\sqrt{3}}{2}yp_x,\ \frac{\sqrt{3}}{2}xp_x - \frac{\sqrt{3}}{2}yp_y - \frac{1}{2}xp_y - \frac{1}{2}yp_x\right]$$

$$= \left[-\frac{1}{2}\left(xp_x - yp_y\right) + \frac{\sqrt{3}}{2}\left(xp_y + yp_x\right),\ -\frac{\sqrt{3}}{2}\left(xp_x - yp_x\right) - \frac{1}{2}\left(xp_y + yp_x\right)\right]$$

$$= \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\frac{\sqrt{3}}{2} & -1/2 \end{bmatrix} \begin{bmatrix} xp_x - yp_y \\ xp_y + yp_x \end{bmatrix}$$

$\chi(C_3) = \underline{-1}$

Transformation properties of elementary functions

$\mathbf{C}_{3v}^{A}$	0	1	2	3
A_1	$^{\square}1$	$^{\square}z$	$x^2+y^2, {}^{\square}z^2$	$^{\square}x(x^2-3y^2), (x^2+y^2)z, {}^{\square}z^3$
A_2		R_z		$^{\square}y(3x^2-y^2)$
E		$^{\square}(x,y), (R_x, R_y)$	$^{\square}(xy, x^2-y^2), {}^{\square}(zx, yz)$	$\{x(x^2+y^2), y(x^2+y^2)\}, {}^{\square}(xz^2, yz^2),$ $^{\square}\{xyz, z(x^2-y^2)\}$

Les harmoniques sphériques en coor. cartésiennes

Moment angulaire	Orbitale	Se transforme comme
$l=0$	$s = Y_0^0$	Invariant (A_1)
$l=1$	$p_z = Y_1^0$	z
	$p_x = \frac{1}{\sqrt{2}}(Y_1^1 - Y_1^{-1})$	x
	$p_y = \frac{1}{i\sqrt{2}}(Y_1^1 + Y_1^{-1})$	y
$l=2$	$d_{z^2} = Y_2^0$	z^2
	$d_{xz} = \frac{1}{\sqrt{2}}(Y_2^1 + Y_2^{-1})$	xz
	$d_{yz} = \frac{i}{\sqrt{2}}(Y_2^1 - Y_2^{-1})$	yz
	$d_{xy} = \frac{i}{\sqrt{2}}(Y_2^2 + Y_2^{-2})$	xy
	$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(Y_2^2 - Y_2^{-2})$	x^2-y^2

Propriétés de transformation d'orbitales

R2

Special Orthogonal group (SO3)

- SO(3) is a the group of all proper rotations about the origin of 3D space.
- In systems of full rotational symmetry, let's take *z* as the axis of rotation.
- The character table is

Each possible rotation forms a class

Infinite number of irreps

SO_3	E	$R(\beta_1)$	$R(\beta_2)$	$\dots$
α_1				
α_2				
$\vdots$				

- The GOT is not helpful for infinite groups
- However, we have already solved analytically this problem: central potential.
- Everything that can exist in SO(3) can be expressed as a sum of spherical harmonics.
- Spherical harmonics can be use to generate the transformation properties of the SO(3).

Spherical harmonics: $$Y_l^m(\theta,\phi) = P_l^m(\theta)e^{im\phi}$$

Rotation β around z: $$R_\beta Y_l^m(\theta,\phi) = P(\theta)e^{im(\phi-\beta)} = e^{-im\beta}Y_l^m(\theta,\phi)$$

Special Orthogonal group (SO3)

For a given l, we have the following diagonal transformation matrix

$$R_\beta \begin{bmatrix} Y_l^l \\ Y_l^{l-1} \\ \dots \\ Y_l^{-l} \end{bmatrix} = \begin{bmatrix} e^{-il\beta} & 0 & \dots & 0 \\ 0 & e^{-i(l-1)\beta} & & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & e^{il\beta} \end{bmatrix} \begin{bmatrix} Y_l^l \\ Y_l^{l-1} \\ \dots \\ Y_l^{-l} \end{bmatrix}$$

The character of this representation is

$$\chi^{(l)}(R(\beta)) = e^{-il\beta} + e^{-i(l-1)\beta} + \dots + e^{il\beta} = \sum_{n=-l}^{l} e^{im_l\beta} = \frac{\sin\left(l+\frac{1}{2}\right)\beta}{\sin\left(\frac{\beta}{2}\right)}$$

From this we can build a character table,

R_3	E	$R(\beta)$	
$D^{(l=0)}$	1	1	Y_0^0
$D^{(l=1)}$	3	$1+2\cos\beta$	(Y_1^{-1}, Y_1^0, Y_1^1)
$D^{(l=2)}$	5	$1+2\cos\beta+2\cos(2\beta)$	$(Y_2^{-2}, Y_2^{-1}, Y_2^0, Y_2^1, Y_2^2)$
$\vdots$	$\vdots$	$\vdots$	
$D^{(l)}$	$2l+1$	$\sum_{m=-l}^{m=l} e^{im\beta}$	

Special Orthogonal group (SO3)

Rotation β + 2π

$$\chi_l(\beta + 2\pi) = \frac{\sin(l + 1/2)(\beta + 2\pi)}{\sin(\beta/2 + \pi)}$$
$$= \frac{\sin(l + 1/2)\beta \cos(l + 1/2)2\pi}{\sin(\beta/2)\cos\pi}$$
$$= (-1)^{2l}\chi_l(\beta)$$

For integer l, nothing usual happens

Rotation β + 4π

$$\chi_l(\beta + 4\pi) = \frac{\sin(l + 1/2)(\beta + 4\pi)}{\sin(\beta/2 + 2\pi)}$$
$$= \frac{\sin(l + 1/2)\beta \cos(l + 1/2)4\pi}{\sin(\beta/2)\cos 2\pi}$$
$$= \chi_l(\beta)$$

Special Unitary group (SU2)

The equation for the characters is also valid for half-integral spins.

Rotation β + 2π $$\chi_{\frac{1}{2}}(\beta + 2\pi) = -1\chi_{\frac{1}{2}}(\beta)$$ *2π rotation is not an invariance*

Rotation β + 4π $$\chi_{\frac{1}{2}}(\beta + 4\pi) = 1\chi_{\frac{1}{2}}(\beta)$$ *4π is!*

Groupe de rotations SO(3) (ou R_3)

Couplage de deux moments angulaires:

Soit deux représentations irréductibles $\Gamma^{(j1)}$ et $\Gamma^{(j2)}$ du groupe R_3 correspondant à des moments angulaires j_1 et j_2. Le produit de ces représentations se décomposera selon une série de Clebsch-Gordan.:

$$\Gamma^{(j_1)} \times \Gamma^{(j_2)} = \Gamma^{(j_1+j_2)} + \Gamma^{(j_1+j_2-1)} + \cdots + \Gamma^{(|j_1-j_2|)}$$

Applications: calculs d'intégrales

Il découle du grand théorème d'orthogonalité que deux fonctions sont orthogonales si elles se transforment comme deux irreps distinctes d'un même groupe.

$$\langle f_i^{(l)} | f_{i'}^{(l')} \rangle \propto \delta_{ii'} \delta_{ll'}$$

l et l' représente deux irreps distinctes
i et i' représente deux composantes d'une irrep multidimensionnelle

Ainsi, le résultat de l'intégral est différent de zéro que si l'intégrant possède une composante appartenant à l'irrep A_1! Physiquement, tous les intégrants dont la représentation ne contient pas A_1 sont impairs par rapport à au moins une variable d'intégration.

Applications: règles de sélections

Ceci est aussi valide pour une intégrale de la forme,

$$\langle \psi^{(l)} | O | \psi^{(l')} \rangle$$

O est un opérateur quelconque
$\psi^{(l)}$ est une fonction d'onde se transformant comme l'irrep l

Ce résultat important permet d'éviter le calcul des éléments de matrice nécessairement égale à zéro pour des raisons de symétrie.

Par exemple, la règle de sélection d'une transition dipolaire électrique est

$$\langle \psi_f | (q\mathbf{r}) | \psi_i \rangle = 0 \text{ si } \Gamma(\psi_f) \cdot \Gamma(q\mathbf{r}) \cdot \Gamma(\psi_i) \not\subset A_1$$

Ainsi, la transition sera interdite si le produit des trois représentations n'inclut pas la représentation infidèle.

Énergie et dégénérescence

Énergie

L'énergie se transforme toujours comme la représentation totalement symétrique, car elle découle de l'hamiltonien.

Dégénérescence

Les fonctions d'onde reliées entre elles par des opérations de symétrie possèdent nécessairement la même énergie. La dégénérescence est donc celle de l'irrep à laquelle la fonction d'onde appartient.