Simmetria e Chimica

Gruppi puntuali e molecole

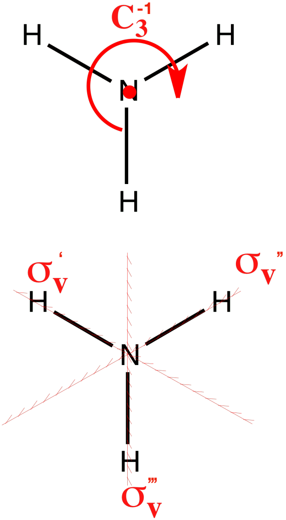
Emanuele Coccia

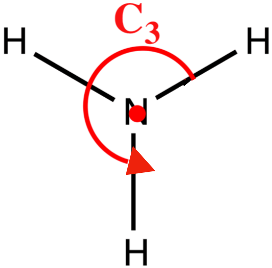
UNIVERSITÀ DEGLI STUDI DI TRIESTE

DSCF Dipartimento di Scienze Chimiche e Farmaceutiche

PhotoInduced Quantum Dynamics (PIQD) Unit

Example: NH_3





Outline

Symmetry Operation

- Operation on an object such that the object is brought into a configuration equivalent to the initial one.
- Indistinguishable.

Symmetry Element

- Geometric entity with respect to which one or more symmetry operations can be defined.
- Rotation axis.
- Plane of symmetry.
- Point (center) of inversion.

Element	Operation(s)	Notation
Symmetry Plane	Reflection	σ
Inversion Center	Inversion regarding the point	i
Rotation Axis	Rotation around the axis	C_n
Improper Axis	Rot. + Refl. in a plane $\perp$	S_n

Symmetry Planes

- The plane must pass through the object.
- If the plane coincides with the XY plane:

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

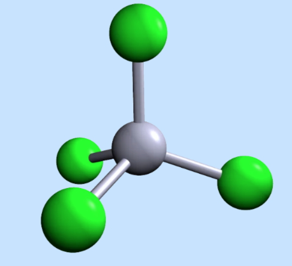
Symmetry Planes

- Atoms on the plane are not moved.
- Atoms of the same type outside the plane occur in pairs.
- If a molecule has only one atom of a given species, that atom must lie on the intersection of all symmetry planes of the molecule.
- Operations generated:

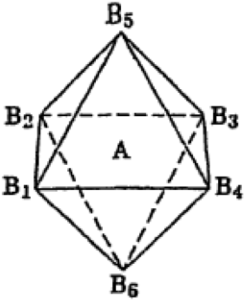
$$\sigma^{2n+1} = \sigma \qquad \sigma^{2n} = E$$

- **Molecules without symmetry planes:**
  - Odd number of all types of atoms, non-planar.
  - Example: CHFClBr (chiral).
- **Molecules with an infinite number of symmetry planes:**
  - Linear molecules.
- **Molecules with one symmetry plane:**
  - F_2SO, Cl_2SO, etc.
- **Molecules with two symmetry planes:**
  - H_2O, CH_2Cl_2 (AB_2C_2 tetrahedral).
- **Molecules with three symmetry planes:**
  - NH_3 (AB_3 pyramidal, except in planar transition state).

- **Molecules with four symmetry planes:**
  - AB_3 planar (SO_3^{2-}, CO_3^{2-}, BF_3, ...).
- **Molecules with five symmetry planes:**
  - AB_4 square planar ($PtCl_4^{2-}$, $AuCl_4^{-}$).
- **Molecules with six symmetry planes:**
  - AB_4 tetrahedral: AB_1B_2, etc.



- **Molecules with nine symmetry planes:**
  - AB_6 octahedral.
  - Three equivalent planes: $AB_1B_2B_3B_4$, etc.
  - Six equivalent planes, of type AB_5B_6 bisecting B_1-B_2 and B_3-B_4, etc.



Center of Inversion

- If the origin coincides with the center:

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

- Only one atom can be at the center (the only one not transformed).
- All other atoms must occur in pairs.
- Generates two operations:

$$i^{2n+1} = i \qquad i^{2n} = E$$

Inversion Center and Inversion Operation

Examples

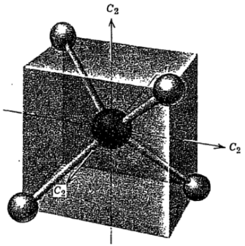
- Octahedral molecules AB_6.
- Square planar molecules AB_4.
- Trans-planar molecules AB_2C_2.
- Linear molecules ABA.
- Ethylene, Benzene.
- **Note:** Tetrahedral AB_4 molecules do **not** have a center of inversion.

Rotation axes of order n

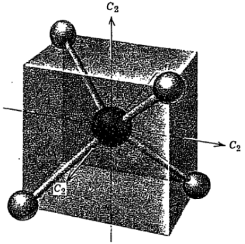
- The symbol used (also for the corresponding operation) is C_n.
- A C_n axis generates n operations:
  - $C_n, C_n^2, C_n^3, \ldots, C_n^n = E$
- An arbitrary number of atoms can lie on the axis.
- If an atom does not lie on the axis, there must be $n-1$ other atoms of the same type (n atoms in total in equivalent positions).

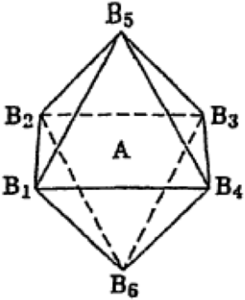
- C_2 generates two operations:
  - $C_2, C_2^2 = E$
- A C_3 axis generates three operations:
  - $C_3, C_3^2 = C_3^{-1}, C_3^3 = E$
- A C_4 axis generates four operations:
  - $C_4, C_4^2 = C_2, C_4^3 = C_4^{-1}, C_4^4 = E$
- A C_6 axis generates six operations:
  - $C_6, C_3, C_2, C_3^2, C_6^{-1}, E$

- **Molecules without rotation axes:**
  - SFClBr, F_2SO, Cl_2SO, ...
- **Molecules with a C_∞ rotation axis:**
  - Linear molecules (all atoms lie on the axis).
- **Molecules with a C_2 rotation axis:**
  - H_2O, CH_2Cl_2, ...
- **Molecules with three C_2 axes:**
  - Ethylene (C_2H_4), Tetrahedral AB_4 molecules.

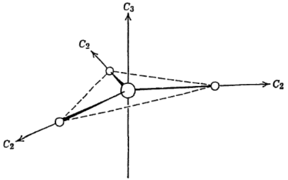


- **Molecules with C_3 rotation axes:**
  - Pyramidal and planar AB_3 molecules.
  - Axis passing through A and $\perp$ to the plane of the three B's.
- **Tetrahedral AB_4 molecules:**
  - Four C_3 axes, passing through A-B bonds.
- **Octahedral AB_6 molecules:**
  - Four axes passing through the centers of two opposite triangular faces and atom A.





- Three C_2 axes coinciding with A-B bonds.
- Consequence of the presence of a C_2 axis perpendicular to the vertical C_3 axis.
- The operations related to C_3 replicate other symmetry elements.



- **Ion $PtCl_4^{2-}$:**
  - Vertical C_4 axis $\perp$ to molecular plane.
  - Four C_2 axes in the plane of the molecular ion.
- **Cyclopentadienyl anion, $C_5H_5^-$:**
  - Vertical C_5 axis.
- **Benzene:**
  - Order 6 axis, $\perp$ to molecular plane.
  - Six C_2 axes in the molecular plane (two sets).

Axes and planes containing the axis C_n, $n = 2, 3, 5, 7$

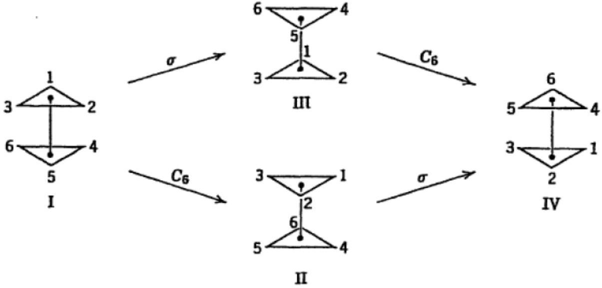
- $C_n, n = 2$:
  - Axes and vertical planes are brought onto themselves.
- $C_n, n = 3, 5, 7$:
  - Generate another $n - 1$ vertical axes and planes.

Axes and planes containing the axis C_n, $n = 4, 6, 8$

- The existence of a vertical plane or C_2 axis requires the presence of a total of $n/2$ such elements.

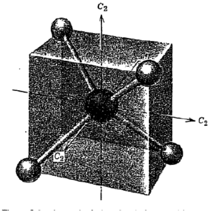
Improper rotation of order n

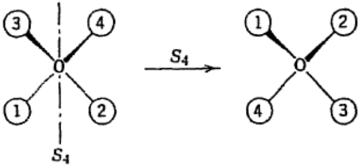
- Symbol: S_n.
- Operation occurs in two steps:
  1. Rotation of $2\pi/n$ regarding the axis.
  2. Reflection in a plane $\perp$ to the axis.
- It exists even when C_n and σ_h are not independent symmetry elements of the object.
- The order of C_n and σ_h is not important.



Three S_4 axes:

- Coinciding with the C_2 axes.





- Assume C_n along Z, σ in XY plane: $[C_n, \sigma] = 0$.
- An improper axis S_n generates operations S_n, S_n^2, $S_n^3, \ldots$
- $S_n^n = (C_n\sigma)^n = C_n^n\sigma^n = E$ (if n is even and σ^n= E).
- $S_n^m = C_n^m$ when m is even.
- **Operations generated by S_6:**
  - S_6, S_6^2, S_6^3, S_6^4, S_6^5, S_6^6
  - $S_6^2 = C_3$; $S_6^3 = S_2 = i$; $S_6^4 = C_3^2$; $S_6^6 = E$.
- The presence of S_{2n} requires the existence of a C_n axis.

Operations generated by element S_n

Improper axis of odd order

- Requires the presence of both σ_h and C_n as independent elements.
- $S_n^n = (C_n\sigma)^n = C_n^n\sigma^n = \sigma$.
- $S_n = C_n\sigma$, so C_n is also a symmetry element.
- S_n generates $2n$ operations.
- Example S_5:
  - S_5, S_5^2=C_5^2, S_5^3, S_5^4=C_5^{-1}, $S_5^5 = \sigma$
  - S_5^6=C_5, S_5^7, S_5^8=C_5^3, S_5^9, $S_5^{10} = E$

Example: $C_2(z) = C_2(y)C_2(x)$

$$C_2(x) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad C_2(y) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$C_2(z) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Matrix multiplication confirms:

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Example: $\sigma_d = C_4(z)\sigma(xz)$

$$\sigma(xz) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad C_4(z) = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_d = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Products of symmetry operations
Matrix Approach

Example: $C_2(z)\sigma(xy) = \sigma(xy)C_2(z) = i$

$$C_2(z) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \sigma(xy) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Multiplication confirms i.

Definition: Elements that are related to each other by symmetry operations of the point group.

Example: Trigonal planar molecule AB_3

- The three C_2 axes are related to each other by C_3 and C_3^2 rotations.
- The three C_2 axes are equivalent.
- The three vertical planes are equivalent:
    - Intersect the molecular plane along the C_2 axes.
    - Related to each other by C_3 and C_3^2 rotations.

- Possesses four C_2 axes in the molecular plane:
  - C_2 and C_2': B-A-B axes.
  - C_2'' and C_2''': bisect the BAB angles.
- Possesses four vertical symmetry planes:
  - Intersect σ_h along the C_2 axes.
- C_2 and C_2' are equivalent (via C_4).
- C_2'' and C_2''' are equivalent to each other.
- C_2 and C_2'' are **not** equivalent elements.
- Vertical planes are equivalent in pairs: $\{\sigma_v, \sigma_v'\}$ and $\{\sigma_d, \sigma_d'\}$.

Equivalent symmetry elements and atoms

Examples

- The three σ_v planes in AB_3 (both planar and trigonal pyramidal) are equivalent:
  - NH_3, BF_3, ...
- The two σ_v planes in H_2O are **not** equivalent.
- The six C_2 axes in the molecular plane of benzene are not all equivalent:
  - 3 axes bisect opposite C-C bonds.
  - 3 axes pass through opposite C atoms.
- The six σ_v planes in benzene are not mutually equivalent (split into two sets).

- Must belong to the same chemical species.
- Are exchanged with each other following any symmetry operation of the point group.

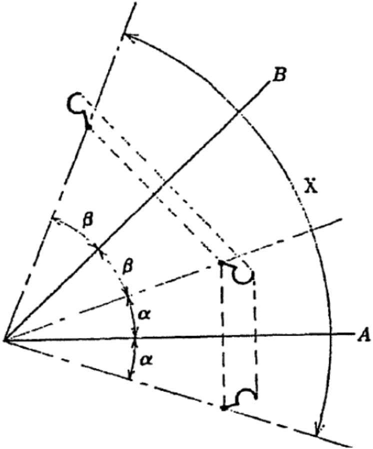
Examples:

- All H atoms in CH_4, C_6H_6, C_2H_4, cyclopropane.
- All F atoms in SF_6.
- All C atoms in $Cr(CO)_6$.
- All O atoms in $Cr(CO)_6$.
- The three equatorial F atoms in PF_5.
- The two axial F atoms in PF_5.

- The product of two proper rotations is a proper rotation (Group of rotations).
- The product of two reflections in planes A and B intersecting at an angle ϕ_{AB} is equivalent to a rotation about the intersection axis by an angle $2\phi_{AB}$.
- Thus, there are a total of $n = \frac{2\pi}{2\phi_{AB}}$ vertical planes.
- Given C_n and a vertical plane, there exist n such planes separated by angle $\phi = \frac{2\pi}{2n}$.
- A C_n axis with n even and a plane $\sigma \perp C_n$ requires the existence of i:

$$C_{2n}^{n}\sigma = \sigma C_{2n}^{n} = C_2\sigma = \sigma C_2 = i$$

- The product of two C_2 rotations regarding two C_2 axes intersecting at an angle θ, is a rotation regarding an axis $\perp$ to the plane of the C_2 axes by an angle 2θ.



- **Two rotations about the same axis:**

$$C_n^k C_n^l = C_n^{k+l}$$

- **Reflections regarding perpendicular planes:**

$$\sigma(xy)\sigma(yz) = \sigma(yz)\sigma(xy) = C_2(y)$$

- **Inversion and any reflection or rotation:** Commute.
- **Two C_2 rotations about perpendicular axes:**

$$C_2(x)C_2(y) = C_2(y)C_2(x) = C_2(z)$$

- **Rotation and reflection in a plane $\perp$ to rotation axis:** Commute.

Every symmetry operation can be expressed in terms of proper or improper rotations:

- $\sigma = E\sigma = C_1^1\sigma = S_1$
- $i = S_2$

Suppose $\sigma = \sigma(xy)$ and $C_2 = C_2(z)$:

$$\hat{\sigma}(xy)\hat{C}_2(z) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \hat{i}$$

Definition and Properties

- **Asymmetric molecules:** Molecules possessing no symmetry elements (Point group C_1).
- **Dissymmetric molecules:** Molecules not superimposable on their mirror image (Chiral).
- All asymmetric molecules are dissymmetric.
- The converse is not necessarily true.

Condition: Dissymmetric molecules do not have S_n symmetry elements.

If an S_n axis exists, the molecule cannot be dissymmetric.

- If S_n of odd order exists, then σ is a symmetry element ($S_n^n = \sigma$).
- If S_n of even order exists and σ does not exist independently:

$$S_n = C_n\sigma \implies C_n^{-1}S_n = \sigma$$

Optical Isomerism

Direct Proposition

If the molecule is not dissymmetric, an S_n axis exists.

- The mirror image must be produced by the symmetry operations of the group.
- Proper rotations cannot produce mirror images. S_n operations are required.
- S_n axes with odd n generate a reflection operation.
- S_2 axis:

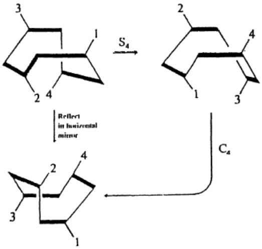
$$S_2 = C_2\sigma = i \implies \sigma = C_2^{-1} i$$

If the molecule is not dissymmetric, an S_n axis exists.

- S_4 axis:
$$S_4 = C_4\sigma \implies \sigma = C_4^{-1}S_4$$
- Mathematical verification using matrices shows relation to reflection.

Example:
1,3,5,7-tetramethylcyclooctatetraene.

- Has an S_4 axis.
- Achiral (not dissymmetric).

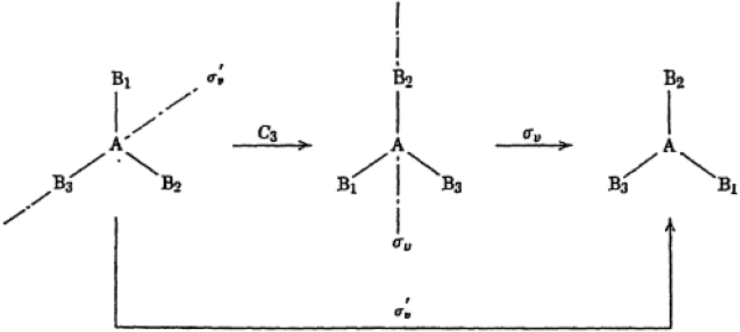


1,3,5,7-tetrametilcicloottatetraene.

For a given molecule, we can compile a list of all symmetry operations compatible with molecular symmetry elements.

Example: Planar AB_3

- Operations: $E, C_3, C_3^{-1}, C_2, C_2', C_2'', \sigma_V, \sigma_V', \sigma_V'', \sigma_h, S_3, S_3^2$.
- This set is closed with respect to the multiplication (composition) of operations.



- The operation E exists in every set.
- Multiplication is associative.
- Every operation possesses an inverse:
  - $\sigma^{-1} = \sigma$, $i^{-1} = i$
  - $(C_n^m)^{-1} = C_n^{n-m}$
- The operation S_n^m always possesses an inverse.

Point Groups Notation

Groups without proper or improper rotation axes

- **Group $\mathbf{C}_1$**: $\{E\}$
  - No symmetry elements: asymmetric molecules.
- **Group $\mathbf{C}_s$**: $\{E, \sigma\}$
  - σ as the unique symmetry element.
- **Group $\mathbf{C}_i$**: $\{E, i\}$
  - i as the unique symmetry element.

- **Group $\mathbf{C}_n$**: $\{C_n, C_n^2, \ldots, C_n^{n-1}, E\}$
  - C_n as unique symmetry element.
  - Cyclic group (ABelian) of order n.
- **Group $\mathbf{S}_n$** ($n > 2$ even): $\{S_n, C_{n/2}, \ldots, S_n^{-1}, E\}$
  - Consists of n operations.
- **Group $\mathbf{C}_{nh}$** (S_n, n odd):
  - Consists of $2n$ operations, including those generated by C_n and σ_h.

- **Group** D_n
  - Axis C_n and n C_2 axes $\perp$ to C_n.
  - Group of order $2n$.
- **Group** C_{nh}
  - Obtained by adding σ_h to vertical axis C_n.
  - $2n$ operations.
- **Group** C_{nv}
  - n vertical planes σ_v.
  - n odd: set of n equivalent σ_v.
  - n even: set of $n/2$ σ_v and $n/2$ σ_d (dihedral).

- Obtained by adding σ_h to D_n.
- $\sigma_h C_n$ generates operations S_n^m.
- $\sigma_h C_2 = \sigma_v$.
- Generators: C_n, σ_h, $n(\sigma_v)$.
- Total $4n$ elements.

- Obtained by adding $n\sigma_d$ to D_n.
- σ_d: Dihedral planes, bisect pairs of C_2 axes.
- n operations generated by products $\sigma_d C_2$.
- Operations generated by S_{2n} collinear with C_n.
- Total $4n$ elements.

- Molecular axis is C_∞.
- Infinite vertical planes σ_v.
- **Molecules with inversion center ($D_{\infty h}$):**
  - Type A-B-A.
  - Additional elements: i, σ_h, $\infty C_2 \perp$ to axis.
- **Molecules without inversion center ($C_{\infty v}$):**
  - Type A-B-C.
  - No other symmetry elements.

Symmetries of regular convex polyhedra (symmetry axes $\perp$ to faces).

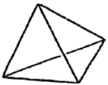
- **Tetrahedron:**
  - Four triangular faces.
  - Four C_3 axes intersecting in the center.

The 5 Regular Convex Polyhedra:

- Equivalent faces (regular polygons).
- Equivalent vertices.
- Equivalent edges.

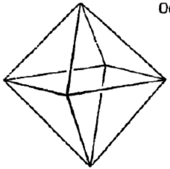
Tetrahedron

- Faces: 4 equilateral triangles
- Vertices: 4
- Edges: 6



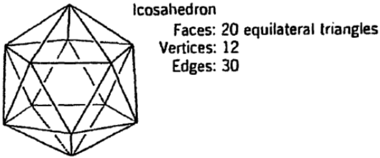
Octahedron

- Faces: 8 equilateral triangles
- Vertices: 6
- Edges: 12



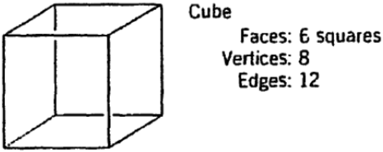
Icosahedron

- Faces: 20 equilateral triangles
- Vertices: 12
- Edges: 30



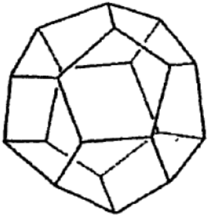
Cube

- Faces: 6 squares
- Vertices: 8
- Edges: 12



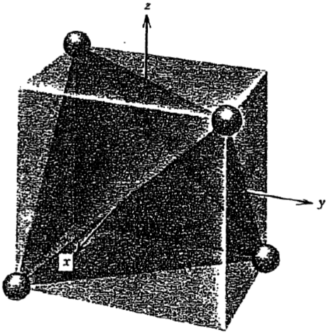
Dodecahedron

- Faces: 12 regular pentagons
- Vertices: 20
- Edges: 30

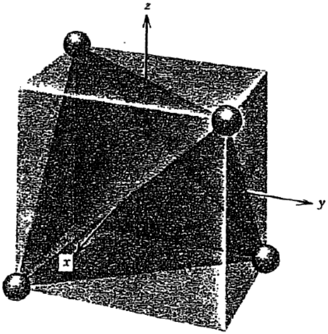


Dodecahedron
Faces: 12 regular pentagons
Vertices: 20
Edges: 30

- Three S_4 axes coinciding with x, y, z.
  - Operations: $S_4, S_4^2 = C_2, S_4^3$.
- Three C_2 axes collinear with S_4.
- Four C_3 axes.
  - Operations: $C_3, C_3^2 = C_3^{-1}$.



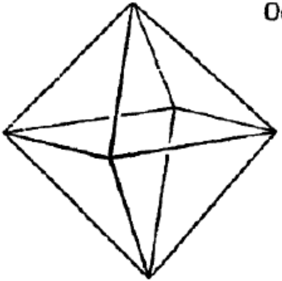
- Six σ_d planes.
- **Group** T_d.
- 24 operations (grouped in classes):
  - $E, 8C_3, 3C_2, 6S_4, 6\sigma_d$.



Octahedron

Symmetry Elements

- Three S_4 axes passing through opposite vertices.
- Three C_2 axes collinear with S_4.
- Three C_4 axes collinear with S_4.
- Six C_2' axes bisecting opposite edges.



Octahedron

Faces: 8 equilateral triangles

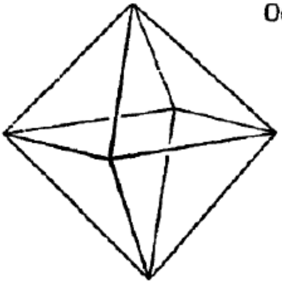
Vertices: 6

Edges: 12

Octahedron

Symmetry Elements

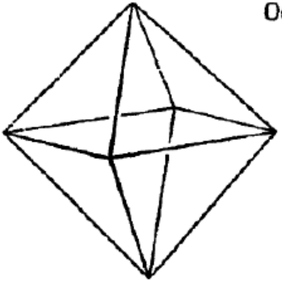
- Four S_6 axes passing through opposite face pairs.
- Four C_3 axes collinear with S_6.
- Center of inversion *i*.
- Three σ_h planes passing through four vertices.



Octahedron

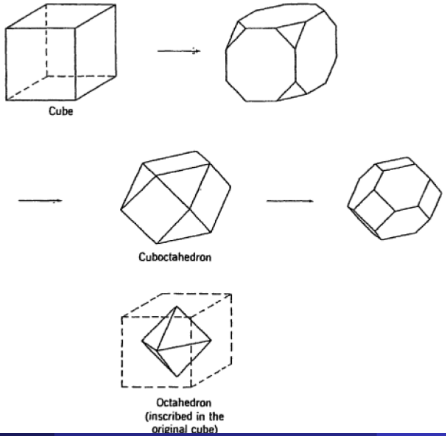
Faces: 8 equilateral triangles
Vertices: 6
Edges: 12

- Six σ_d planes passing through opposite vertices and bisecting edges.
- **Group** O_h.
- 48 operations:
    - $E, 8C_3, 6C_2, 6C_4, 3C_2(= C_4^2), i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d$.

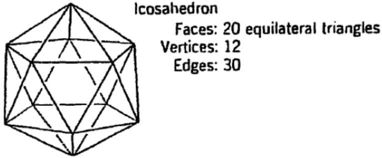


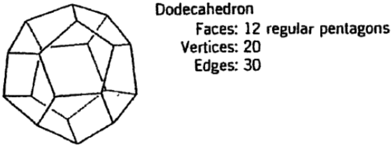
Octahedron
Faces: 8 equilateral triangles
Vertices: 6
Edges: 12

- Group O_h same as transitional solids.
- Cube: faces penetrated by C_4, vertices by C_3.
- Octahedron: faces penetrated by C_3, vertices by C_4.
- Cuboctahedron.



- Six S_{10} axes.
  - Dodecahedron: through opposite pentagonal faces.
  - Icosahedron: through opposite vertices.
- Operations generated: $S_{10}, C_5, S_{10}^3, C_5^2, i, \ldots$

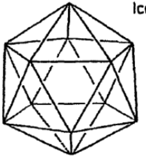




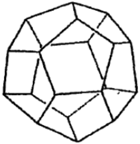
Dodecahedron and Icosahedron

Elements

- Ten S_6 axes.
  - Dodecahedron: through opposite vertices.
  - Icosahedron: through opposite faces.
- Operations: $S_6, C_3, i, \ldots$

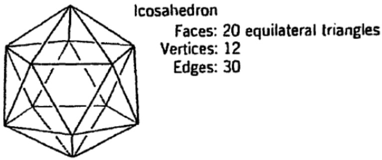


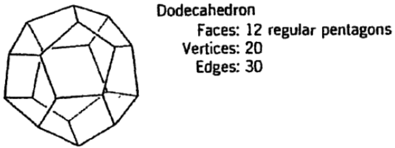
Icosahedron
Faces: 20 equilateral triangles
Vertices: 12
Edges: 30



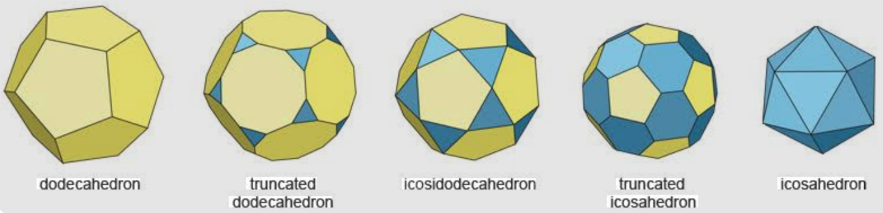
Dodecahedron
Faces: 12 regular pentagons
Vertices: 20
Edges: 30

- Six C_5 axes collinear with S_{10}.
- Ten C_3 axes collinear with S_6.
- Fifteen C_2 axes bisecting opposite edges.
- Fifteen planes σ.





- **Group** I_h.
- 120 operations.
- Includes E, $12C_5$, $12C_5^2$, $20C_3$, $15C_2$, i, $12S_{10}$, $20S_6$, 15σ.



- Obtained by removing reflection and improper rotation operations from T_d, O_h, I_h.
- **Group T**: 12 operations $(E, 4C_3, 4C_3^2, 3C_2)$.
- **Group O**: 24 operations $(E, 8C_3, 6C_2, 6C_4, 3C_2)$.
- **Group I**: 60 operations $(E, 12C_5, 12C_5^2, 20C_3, 15C_2)$.

Group T_h
Operations

- Obtained by adding a set of planes σ_h containing the C_2 axes to Group T.
- Includes center of inversion i.
- Operations: $E, 4C_3, 4C_3^2, 3C_2, i, 4S_6, 4S_6^5, 3\sigma_h$.

Classification Procedure

Step 1: Special Groups

- Linear molecules: $C_{\infty v}$ or $D_{\infty h}$.
- High symmetry (multiple high-order axes): T_d, O_h, I_h (or subgroups T, T_h, O, I).

Step 2: No proper/improper axes?

- Only plane $\sigma \implies C_s$.
- Only inversion $i \implies C_i$.
- No elements $\implies C_1$.

Step 3: Only S_n (even)?

- Group S_n (rare).

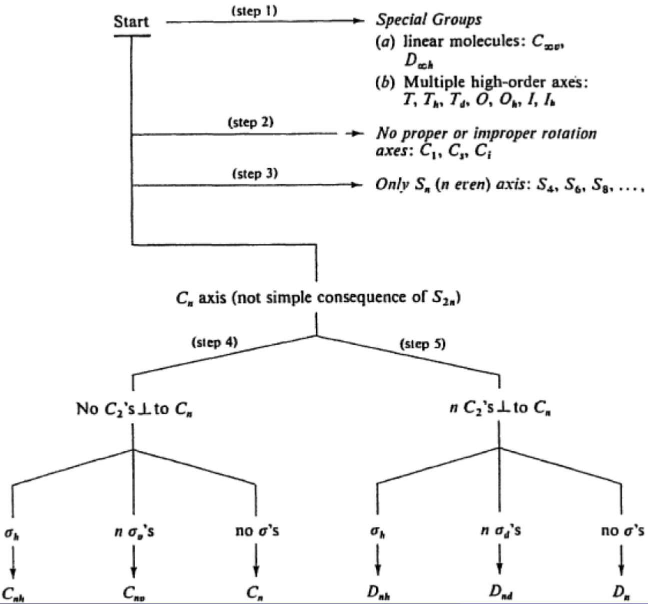
Classification Procedure

Step 4: Exists C_n, but no $nC_2 \perp C_n$

- No other elements $\implies C_n$.
- Exists $n\sigma_v \implies C_{nv}$.
- Exists $\sigma_h \implies C_{nh}$.

Step 5: Exists C_n AND $nC_2 \perp C_n$

- No other elements $\implies D_n$.
- Exists $\sigma_h \implies D_{nh}$.
- Exists $n\sigma_d \implies D_{nd}$.


Start
(step 1)
Special Groups
(a) linear molecules: C∞v, D∞h
(b) Multiple high-order axes: T, Th, Td, O, Oh, I, Ih
(step 2)
No proper or improper rotation axes: C1, Cs, Ci
(step 3)
Only Sn (n even) axis: S4, S6, S8, . . . ,
Cn axis (not simple consequence of S2n)
(step 4)
(step 5)
No C2's ⊥ to Cn
n C2's ⊥ to Cn
σh
n σv's
no σ's
σh
n σd's
no σ's
Cnh
Cnv
Cn
Dnh
Dnd
Dn

Example: H_2O

Group C_{2v}

- No S_n axes.
- 1 proper rotation axis C_2.
- 2 σ planes containing the C_2 axis:
  - Molecular plane.
  - Plane bisecting H-H.

Example: NH_3

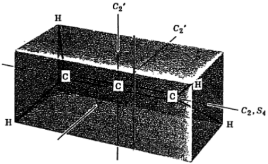
Group C_{3v}

- No S_n axes.
- 1 proper rotation axis C_3.
- 3 σ_v planes intersecting at C_3.

Example: Allene

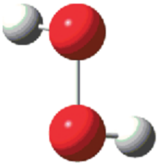
Group D_{2d}

- S_4 axis coincides with molecular axis.
- Two C_2 axes orthogonal to vertical axis.
- Two vertical symmetry planes σ_d.

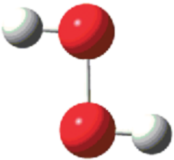


Group C_2

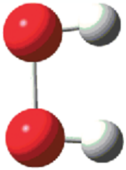
- Equilibrium configuration ($\theta \neq 0, 90°$).
- 1 vertical C_2 axis.
- No planes of symmetry.
- No S_n.



(I) Open book



(II) Trans

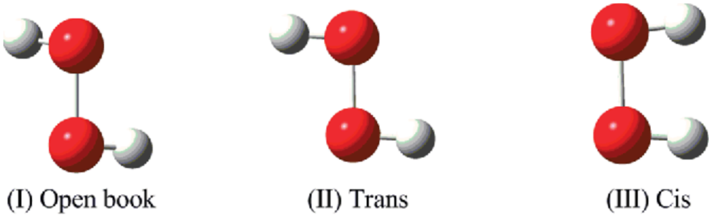


(III) Cis

Example: H_2O_2 (Cis-planar)

Group C_{2v}

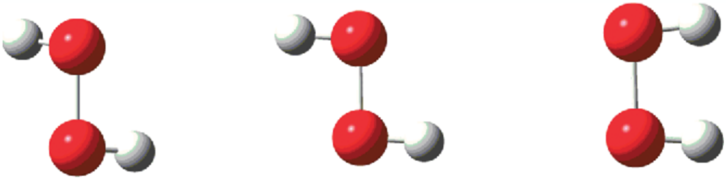
- $\theta = 0°$.
- 1 vertical C_2 axis.
- 2 vertical planes (Molecular plane, Bisecting plane).



Example: H_2O_2 (Trans-planar)

Group C_{2h}

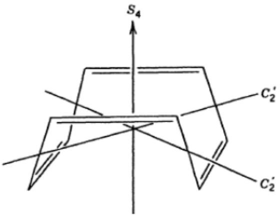
- $\theta = 180°$.
- 1 vertical C_2 axis.
- 1 σ_h (molecular plane).
- Center of inversion i.

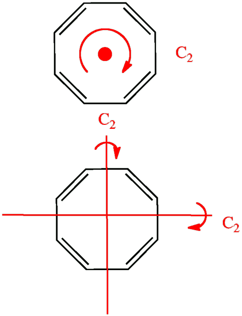


(I) Open book (II) Trans (III) Cis

Group D_{2d}

- Tub shape.
- 1 S_4 axis.
- 1 C_2 axis coincident with S_4.
- 2 C_2' axes $\perp$ to vertical.
- 2 vertical planes.

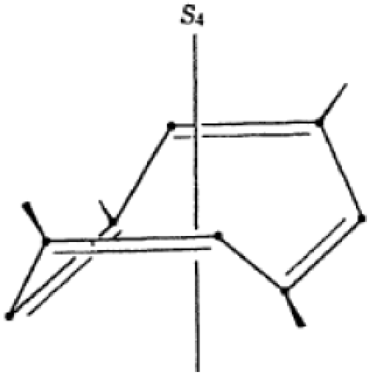




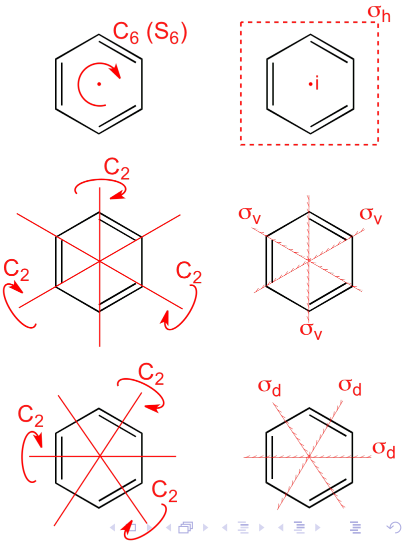
Example: 1,3,5,7-Tetramethylcyclooctatetraene

Group S_4

- 1 improper axis S_4.
- No other symmetry elements.
- Methyl groups lower the symmetry.



Benzene D_{6h}



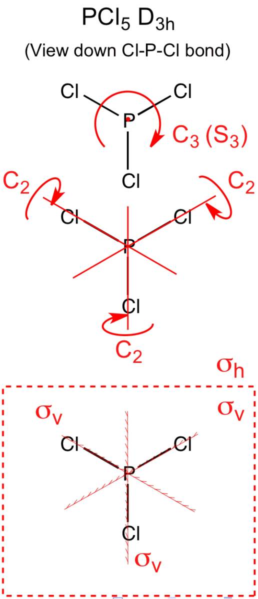
Group D_{6h}

- Vertical C_6 and S_6.
- 6 C_2 axes in the ring plane.
- σ_h.
- i.
- 3 σ_v and 3 σ_d.

Example: PCl_5 (Trigonal bipyramidal)

Group D_{3h}

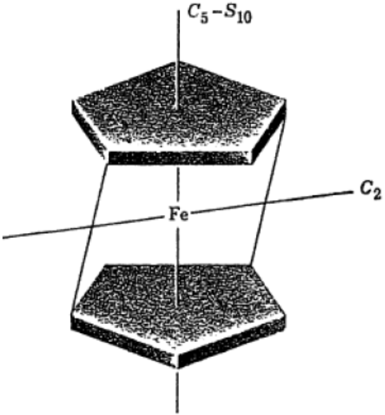
- 1 C_3 axis.
- 3 C_2 axes (equatorial bonds).
- 3 σ_v.
- 1 σ_h.



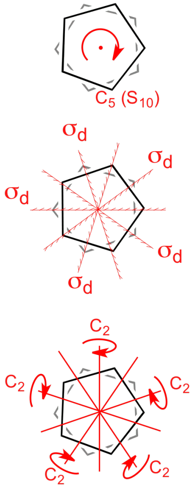
Example: Ferrocene (Staggered)

Group D_{5d}

- C_5 and S_{10} axis, 5 C_2 axes, 5 σ_d, i.

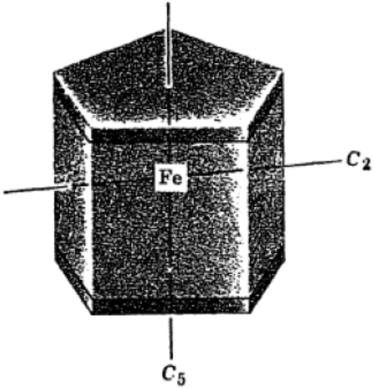


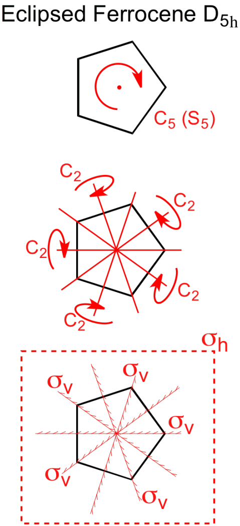
Staggered Ferrocene D5d



Group D_{5h}

- C_5 axis, 5 C_2 axes, 5 σ_v, σ_h.





Example: Ferrocene (Other configurations)

Group D_5

- 1 C_5 axis.
- 5 C_2 axes.
- No planes of symmetry.