① The elementary properties of groups

1.1 Basic definitions

Def: BINARY COMPOSITION is a law that associates to two abstract elements g_i and g_j of a set $\mathcal{G}$ a third element g_k

ex. . set of natural numbers with the sum
. set of real numbers with the product
. set of functions $f: \mathbb{R} \to \mathbb{R}$ with composition $f \circ g(x) = f(g(x))$
. set of square matrices with matrix multiplication

Def: GROUP is a set $\mathcal{G}$ of elements and a binary composition $(\cdot)$ satisfying the following 4 properties

1. $A \in \mathcal{G}$ and $B \in \mathcal{G} \Rightarrow A \cdot B \in \mathcal{G}$
2. $\forall A, B, C \in \mathcal{G} \quad (A \cdot B) \cdot C = A \cdot (B \cdot C)$
3. $\forall A \in \mathcal{G} \ \exists E \in \mathcal{G}: \ E \cdot A = A$
4. $\forall A \in \mathcal{G} \ \exists A^{-1} \in \mathcal{G}: \ A^{-1} \cdot A = E$

In words: 1. $\mathcal{G}$ is closed with respect to $\cdot$; 2. The associative law holds true 3. $\mathcal{G}$ contains the identity 4. Every element of $\mathcal{G}$ has an inverse in $\mathcal{G}$.

Notice that the binary composition is normally indicated in group theory with the multiplication symbol $(\cdot)$.

Observations to the 3^{rd} and 4^{th} axiom in the definition of a group: given the four axioms it follows that

- A^{-1} is uniquely defined and $A \cdot A^{-1} = E$
- E is uniquely defined and $A \cdot E = A$

proof: let us take A^{-1} and $(A^{-1})^{-1}$: $A^{-1}\cdot A = E$ and $(A^{-1})^{-1}\cdot A^{-1} = E$

- $$A\cdot A^{-1} = E\cdot(A\cdot A^{-1}) = [(A^{-1})^{-1}\cdot A^{-1}]\cdot(A\cdot A^{-1}) =$$
$$= (A^{-1})^{-1}\cdot \underbrace{(A^{-1}\cdot A)}_{E}\cdot A^{-1} = (A^{-1})^{-1}\cdot A^{-1} = E.$$

- $$E\cdot A = (A\cdot A^{-1})\cdot A = A\cdot(A^{-1}\cdot A) = A\cdot E = A$$

- $\exists\, E_1$ and E_2 satisfying the axioms $\Rightarrow$ $E_1 = E_1E_2 = E_2$
- $\exists\, (A^{-1})_1$ and $(A^{-1})_2$ $\Rightarrow$ $(A^{-1})_1\cdot A\cdot(A^{-1})_2 = \begin{cases} (A^{-1})_1 E = (A^{-1})_1 \\ E(A^{-1})_2 = (A^{-1})_2 \end{cases}$

Notice that, in general, $A\cdot B \neq B\cdot A$. If $A\cdot B = B\cdot A$ the group is called abelian

Def: ORDER of a group is the number of elements contained into the group.

Def: CONJUGATE ELEMENTS: if $A, B, C \in \mathcal{G}$ and $ABA^{-1} = C \Rightarrow C$ is called the transform of B through A and B and C are conjugate elements.

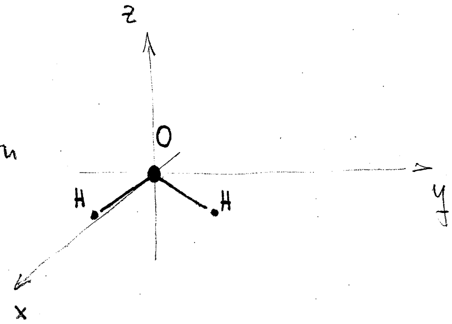
Def: CLASS: the complete set of elements conjugate to A (within a group $\mathcal{G}$) forms the class $\mathcal{C}_A$. The number of elements in the class is called order of the class.

1.2| Multiplication table and rearrangement theorem

$\cdot$	group elements
group elements	results of the multiplication

Example of multiplication table for the symmetry group of the water molecule

The symmetry operations that leave the water molecule into a indistinguishable configuration



C_2 rotation of π around the z axis

σ_{yz}, σ_{xz} } mirror reflection with respect to the plane xz or yz

The product consist in applying the two operations in a row from right to left.

$\cdot$	E	C_2	σ_{yz}	σ_{xz}
E	E	C_2	σ_{yz}	σ_{xz}
C_2	C_2	E	σ_{xz}	σ_{yz}
σ_{yz}	σ_{yz}	σ_{xz}	E	C_2
σ_{xz}	σ_{xz}	σ_{yz}	C_2	E

- symmetric <=> Abelian group
- each group element in the rows and column

$\downarrow$

<u>Theorem</u>. REARRANGEMENT THEOREM: If $g_1, \dots, g_h$ are the elements of a group $\mathcal{G}$ of order h and taken g_k $1 \le k \le h$, then the set of elements

$$\mathcal{S} = \{ g_k g_1, \dots, g_k g_h \}$$

coincides with $\mathcal{G}$.

<u>proof</u>:
- $\mathcal{G} \subseteq \mathcal{S}$ $\quad g_i \in \mathcal{G} \to \exists\, g_r = g_k^{-1} \cdot g_i \in \mathcal{G} \Rightarrow g_i = g_k g_r \Rightarrow g_i \in \mathcal{S}$
- $\mathcal{S} \subseteq \mathcal{G}$ all elements of $\mathcal{S}$ have the form $g_k g_i \Rightarrow$ they belong to $\mathcal{G}$ since g_k and $g_i \in \mathcal{G}$. ■

Def: HOMOMORPHISM: a mapping $f: \mathcal{G} \to \mathcal{G}'$ respecting the multiplication

$$f(A \cdot B) = f(A) * f(B)$$

where $*$ is the multiplication in $\mathcal{G}'$.

Def ISOMORPHISM: a homomorphism between two groups $\mathcal{G}$ and $\mathcal{G}'$ of the same order such that $\forall A' \in \mathcal{G}' \ \exists! A \in \mathcal{G} : A' = f(A)$.

Two groups with the same multiplication table are isomorphic and represent the same abstract group.

1.3| Subgroups and cosets

Def SUBGROUP: collection of elements within a group which by themselves form a group.

Theorem: For every element g of a group $\mathcal{G}$ of finite order one can find a natural number n fulfilling the relation $g^n = E$

proof: A number of multiplications larger than the order of the group MUST give rise to repetitions $\Rightarrow$ we can find p, q such that

$$g^p = g^q \qquad \text{and} \qquad p > q$$

$$\Rightarrow \quad g^q = g^p = g^{q+n} = g^n \cdot g^q \quad \Rightarrow \quad g^n = E$$

∎

Def ORDER OF AN ELEMENT is the smallest value of n in the relation $g^n = E$

Theorem: For element g of a group $\mathcal{G}$ of finite order one can construct the subgroup:

$$S_g = \{g, g^2, \dots, g^n\}$$

where n is the order of g. S_g is called cyclic subgroup of $\mathcal{G}$ with generator g.

The group of the water molecule contains 3 cyclic subgroups of order 2 with generators C_2, σ_{xz}, σ_{yz}.

Def COSET : If $\mathcal{B}$ is a subgroup of $\mathcal{G}$ and $g \in \mathcal{G}$ $\Rightarrow \{g b_1, \dots, g b_n\}$ is the left coset of $\mathcal{B}$ with respect of g.

The left (or right, analogously) cosets are not subgroups, unless $g \in \mathcal{B}$.

Theorem Two left (right) cosets either contain exactly the same elements or else have no element in common.

proof : $g_1 \mathcal{B} \cap g_2 \mathcal{B} \neq \emptyset \Rightarrow \exists\ b_n$ and b_m : $g_1 b_n = g_2 b_m$

$$\Rightarrow g_2^{-1} \cdot g_1 = b_m b_n^{-1} \iff g_2^{-1} g_1 \in \mathcal{B}$$

$$\Rightarrow g_2^{-1} g_1 \mathcal{B} = \mathcal{B} \Rightarrow g_1 \mathcal{B} \equiv g_2 \mathcal{B}$$

■

One can deduce an important consequence on the order of the subgroups

Theorem The order of a subgroup is a divisor of the order of the group

proof Let $\mathcal{G}$ be a group of order h
Let $\mathcal{B}$ be a subgroup of order l

We construct all possible cosets $\mathcal{B} g_i$ with $g_i \in \mathcal{G}$. The number of element in each coset is always l. Only a finite number (m) of distinct cosets can be formed within $\mathcal{G}$ and they cannot share elements.

$$\Rightarrow h = m l$$

■

The group of the water molecule has only subgroups of order 1, 2, 4.

$\{E\}$ $\{E, C_2\}$, $\{E, \sigma_{xz}\}$, $\{E, \sigma_{yz}\}$ $\{E, C_2, \sigma_{xz}, \sigma_{yz}\}$

1.4 Symmetry operations and point groups

The groups that we consider in this context are composed of symmetry operations

Def: SYMMETRY OPERATION is an operation that leaves an object in an indistinguishable configuration which is said to be equivalent.

Among other symmetry operations, the ones needed for studying finite size objects (as for example molecules) are point symmetry operations

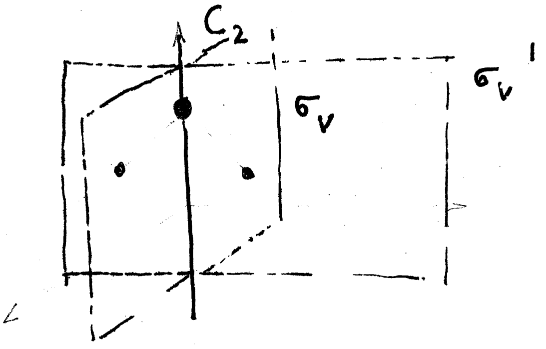
Def: POINT SYMMETRY OPERATIONS are symmetry operations keeping at least 1 point invariant in space.

Nomenclature

- E identity (from german Einheit) preserves the entire space
- C_n (proper) rotation of $\frac{2\pi}{n}$ radians around a certain axis.
  The axis with the larger n is called principal axis.
  Twofold axes perpendicular to the principal axis are called dihedral and are denoted by C_2' or C_2''. C_n (C_2', C_2'') preserves a line.
- σ mirror operation (σ from Spiegel = mirror) with respect to a plane
  - σ_h the mirror plane is perpendicular to the principal axis
  - σ_v the mirror plane contains the principal axis
  - σ_d special case of σ_v with the plane bisecting the angle formed by 2 dihedral axes.
- i inversion with respect to a point
- S_n rotation of $\frac{2\pi}{n}$ around a certain axis followed by a reflection with respect to a plane perpendicular to the rotation axis.

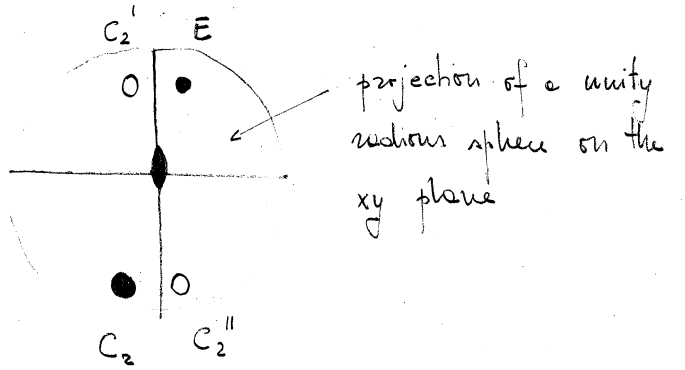
Def : SYMMETRY ELEMENT is a point, a line, or a plane with respect of which a point symmetry operation is carried out.

Example: The water molecule has 3 symmetric elements: i.e. a twofold symmetry axis C_2 and 2 vertical planes $\sigma_v = \sigma_{xz}$ and $\sigma_v' = \sigma_{yz}$.



Def : POINT GROUP a group whose elements are point symmetry operations

Projection diagrams are useful pictorial representations of point groups



● point in the upper hemisphere

o point in the lower hemisphere

The order of the principal rotation is given by a poligon in the center

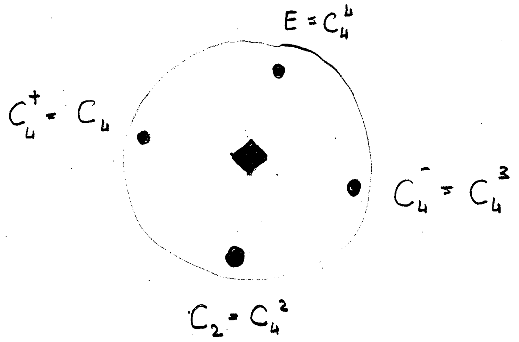
C_2 △ C_3 □ C_4 ...

Point groups are distinguished into 2 major groups of proper and improper ones. Proper point groups only consist of rotations.

PROPER GROUPS

(i) Cyclic groups: C_n There is only 1 axis of rotation and the group elements are C_n^k $k = 1, \dots, n$. Order $= n$

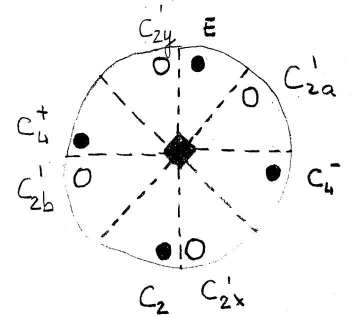
Example C_4



(ii) Dihedral groups D_n: Proper rotations that transform a regular n-sided prism into itself. The symmetry elements are C_n and nC_2'

Order $= 2n$

Example D_4

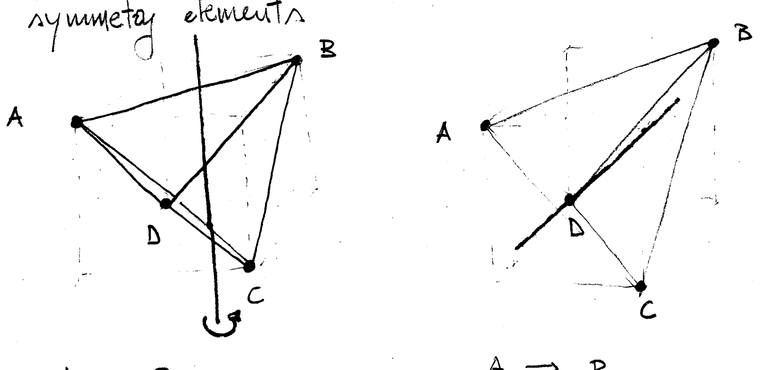


$a = [1\,1\,0]$

$b = [\bar{1}\,1\,0]$

(iii) Tetrahedral group: T Proper rotations that transform a tetrahedron into itself The symmetry elements are $3C_2$ and $4C_3$. The order 12

Examples of symmetry elements



C_2	C_3
$A \to B$	$A \to B$
$B \to A$	$B \to C$
$C \to D$	$C \to A$
$D \to C$	$D \to D$

(iv) Octahedral or cubic group: O Proper rotations that transform an octahedron or a cube into itself. The symmetry elements $3C_4$ $4C_3$ $9C_2$

Order $= 1 + 6 + 8 + 9 = 24$

(v) Icosahedral group: Y Proper rotations that transform an icosahedron or pentagonal dodecahedron in itself. The symmetry elements are

$6C_5$ $10C_3$ $15C_2$ The order $= 1 + 24 + 20 + 15 = 60$

Understandable since the dodecahedron has

12 pentagonal faces parallel in pairs
20 threefold vertices opposite with respect of the center
30 edges $V - E + F = 2$

$V =$ number of vertices, $E =$ number of edges, $F =$ number of faces — opposite with respect to the center

Notice: The fullerene molecule C_{60} as a truncated icosahedron has a Y symmetry. More properly C_{60} has a larger symmetry group Y_h due to the inversion i

For the understanding of the improper groups it is useful to introduce the concept of direct product of 2 groups.

Def: DIRECT PRODUCT a group $\mathcal{G}$ is the direct product of 2 subgroups $\mathcal{G}_a$ and $\mathcal{G}_b$ $\mathcal{G} = \mathcal{G}_a \otimes \mathcal{G}_b$ if

- $A \cdot B = B \cdot A$ $\forall$ $A \in \mathcal{G}_a$ and $B \in \mathcal{G}_b$
- $\mathcal{G}_a \cap \mathcal{G}_b = E$
- every element of $\mathcal{G}$ can be written as $A \cdot B$ with $A \in \mathcal{G}_a$ and $B \in \mathcal{G}_b$

Now we consider the group $C_i = \{E, i\}$ and construct $C_i \otimes \mathcal{G}$ where $\mathcal{G}$ is each of the proper groups introduced so far. It is not difficult to convince yourself that i commutes with all proper rotations since i is represented in $\mathbb{R}^3$ by the matrix $-\mathbb{1}_3$, which commutes with any other matrix.

IMPROPER GROUPS

(i) From C_n - if n is odd $C_n \otimes C_i = S_{2n}$

- if n is even $C_n \otimes C_i = C_{nh}$

where h stands for horizontal reflection plane which arises since $i \cdot C_2 = \sigma_h$

(ii) From D_n - if n is odd $D_n \otimes C_i = D_{nd}$

d denotes dihedral planes bisecting the angles between C_2' dihedral axes

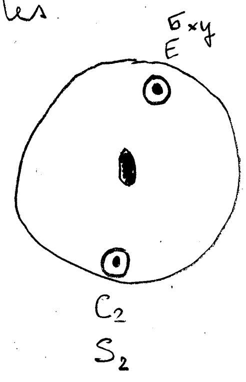
- if n is even $D_n \otimes C_i = D_{nh}$

(iii) $T \otimes C_i = T_h$

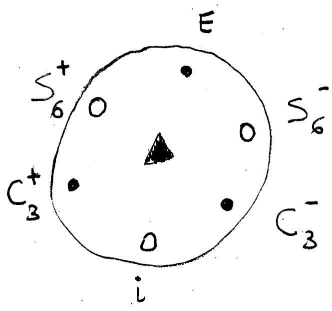
(iv) $O \otimes C_i = O_h$

(v) $Y \otimes C_i = Y_h$

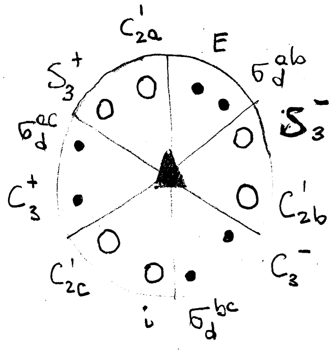
Examples.



$C_{2h} = C_2 \otimes C_i$



$S_6 = C_3 \otimes C_i$



$D_{3d} = D_3 \otimes C_i$

T_d, the full symmetry group of the tetrahedron is isomorphic to the cubic group O (to be proven)

1.5 Identification of molecular point group

Linear molecules

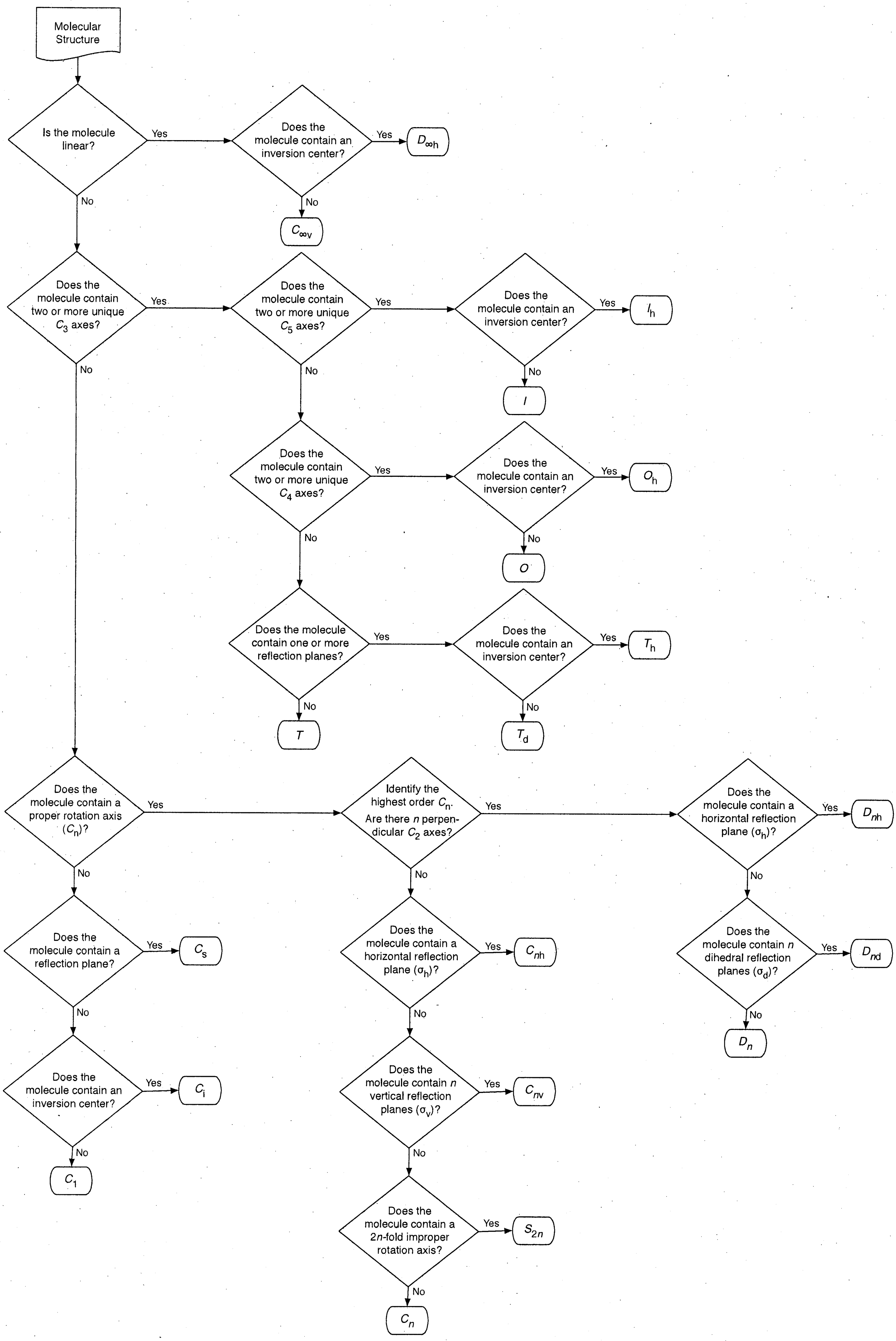
- no σ_h → $C_{\infty v}$ (ex. H-Cl)
- σ_h → $D_{\infty h}$ (ex O=C=O)

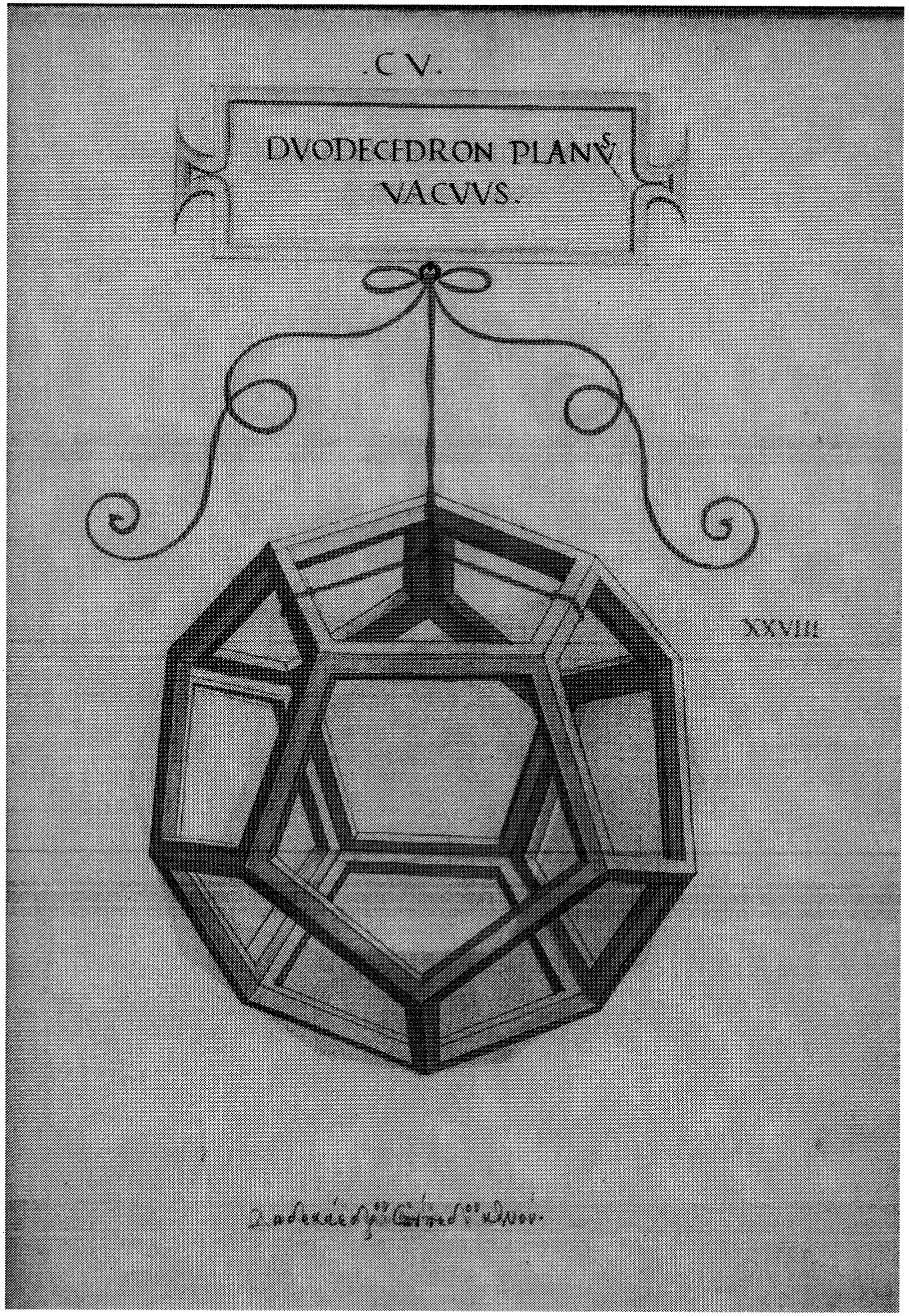
Non-linear molecules

- no proper rot axis
  - σ — $C_s = \{E, \sigma\}$
  - i — C_i
  - neither σ nor i — C_1
- C_n $n > 1$
  - $\leq 1 C_3$
    - $n C_2' \perp C_n$
      - σ_h — D_{nh} (ex. Benzene)
      - $n\sigma_d$ — D_{nd}
      - no σ — D_n
    - no $C_2' \perp C_n$
      - σ_h — C_{nh}
      - $n\sigma_v$ — C_{nv}
      - i, no σ — S_{2n}
      - no i no σ — C_n
  - $> 1 C_3$
    - $4 C_3$
      - $3 S_4$ — T_d (Methane)
      - $3 C_4$
        - i — O_h
        - no i — O
      - $3 C_2$
        - i — T_h
        - no i — T
    - $10 C_3, 6 C_5$
      - i — Y_h (C_{60})
      - no i — Y

symmetry.otterbein.edu

As one can see from the diagram above the presence of reflection symmetries introduces C_s, C_{nv}, C_{nh} (n, odd), D_{nd}, D_{nh} (n odd), T_d


Molecular Structure
Is the molecule linear?
Yes
No
Does the molecule contain an inversion center?
Yes
No
$D_{\infty h}$
$C_{\infty v}$
Does the molecule contain two or more unique C_3 axes?
Does the molecule contain two or more unique C_5 axes?
Does the molecule contain an inversion center?
I_h
I
Does the molecule contain two or more unique C_4 axes?
Does the molecule contain an inversion center?
O_h
O
Does the molecule contain one or more reflection planes?
Does the molecule contain an inversion center?
T_h
T
T_d
Does the molecule contain a proper rotation axis (C_n)?
Identify the highest order C_n. Are there n perpendicular C_2 axes?
Does the molecule contain a horizontal reflection plane (σ_h)?
D_{nh}
Does the molecule contain n dihedral reflection planes (σ_d)?
D_{nd}
D_n
Does the molecule contain a reflection plane?
C_s
Does the molecule contain an inversion center?
C_i
C_1
Does the molecule contain a horizontal reflection plane (σ_h)?
C_{nh}
Does the molecule contain n vertical reflection planes (σ_v)?
C_{nv}
Does the molecule contain a $2n$-fold improper rotation axis?
S_{2n}
C_n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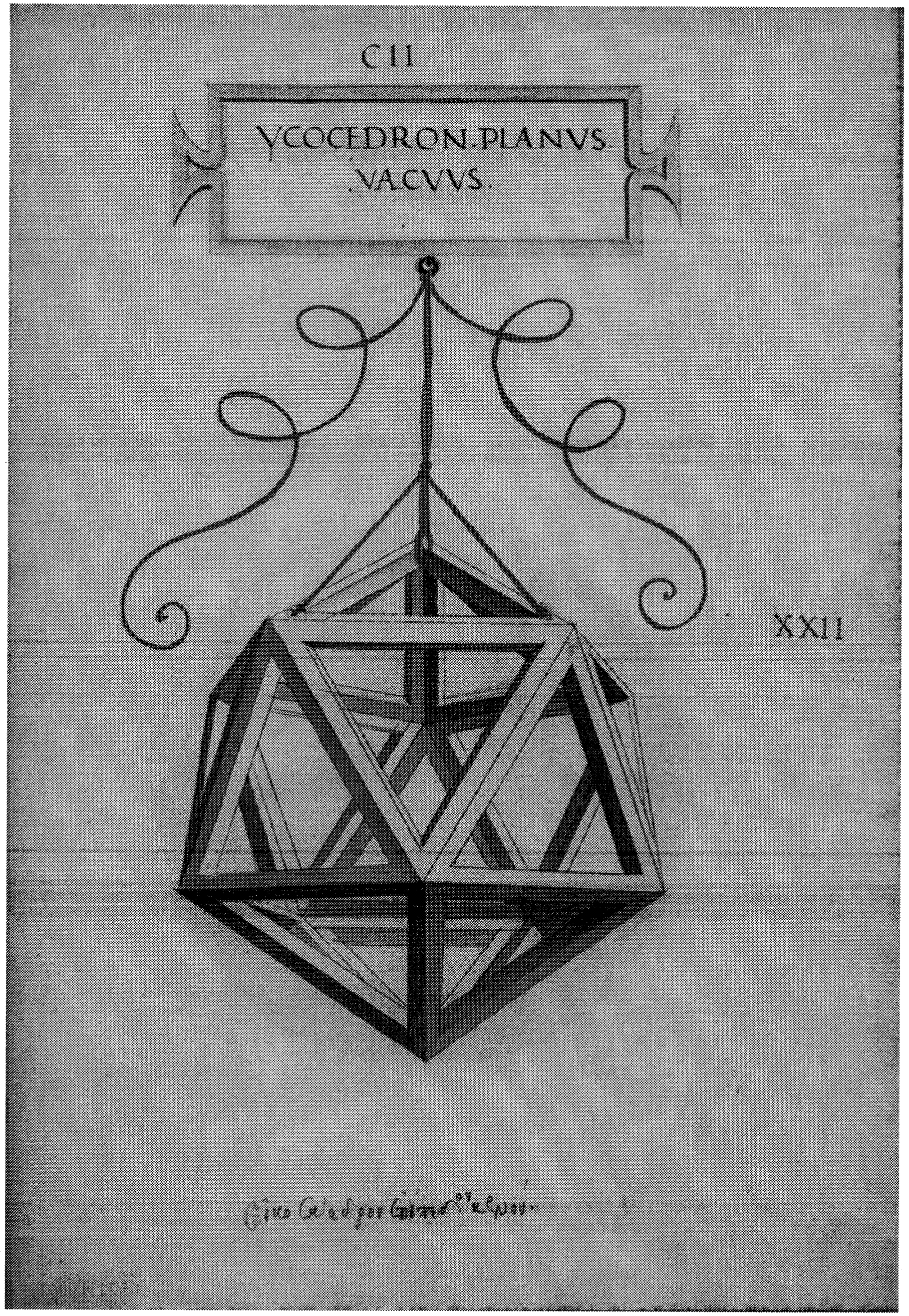
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