Elements and Operations

☞ A **symmetry element** is an imaginary geometrical construct about which a symmetry operation is performed.

☞ A **symmetry operation** is a movement of an object about a symmetry element such that the object's orientation and position before and after the operation are indistinguishable.

- ✓ A symmetry operation carries every point in the object into an **equivalent** point or the **identical** point.

Point Group Symmetry

- ☞ All symmetry elements of a molecule pass through a central point within the molecule.
- ☞ The more symmetry operations a molecule has, the higher its symmetry is.
- ☞ Regardless of how many or few symmetry operations a molecule possesses, all are examples of one of five types.

Operation	Element	Element Construct
Identity, E	The object	N/A
Proper rotation, C_n	Proper axis, Rotation axis	line
Reflection, σ	Mirror plane, Reflection plane	plane
Inversion, i	Inversion center, Center of symmetry	point
Rotation-reflection Improper rotation, S_n	Improper axis, alternating axis	line

Proper Rotation, C_n

☞ If a molecule has rotational symmetry, rotation by $2\pi/n = 360°/n$ brings the object into an equivalent position.

- ✓ The value of n is the **order** of an n-fold rotation.

- ✓ If the molecule has one or more rotational axes, the one with the highest value of n is the **principal axis of rotation**.

Fig. 1.1 Successive C_4 clockwise rotations of a planar MX_4 molecule about an axis perpendicular to the plane of the molecule ($X_A = X_B = X_C = X_D$).

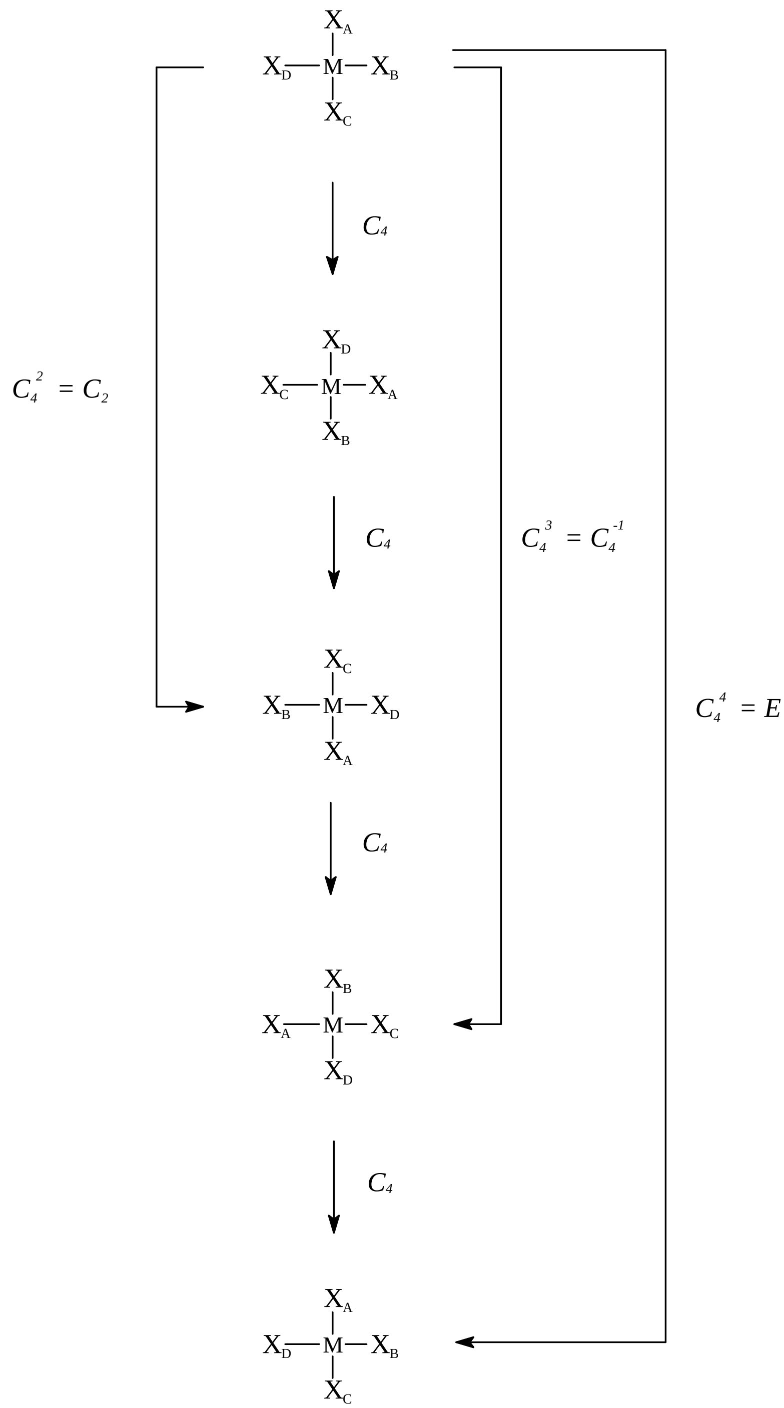
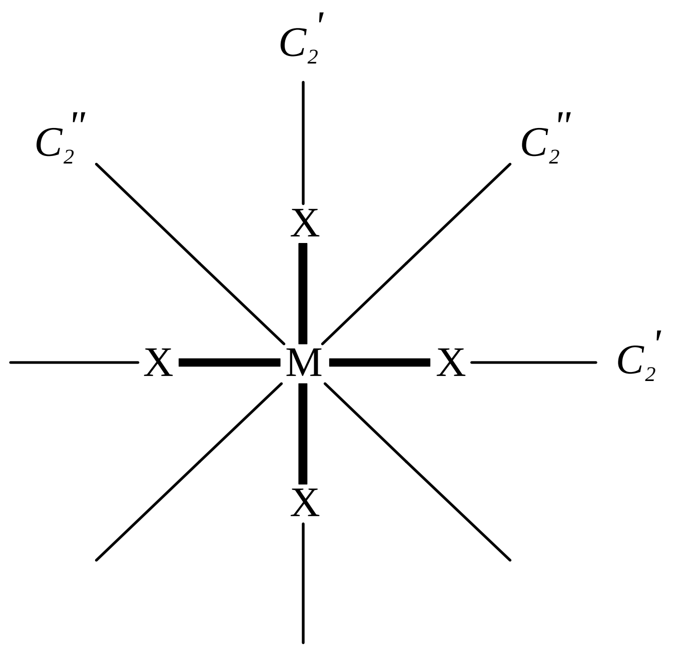


Fig. 1.2 The C_2' and C_2'' axes of a planar MX_4 molecule.



General Relationships for C_n

$$C_n^{\,n} = E$$

$$C_n^{\,n/2} = C_2 \;\; (n \text{ even})$$

$$C_n^{\,n-1} = C_n^{\,-1}$$

$$C_n^{\,n+m} = C_n^{\,m} \;\; (m < n)$$

✓ Every n-fold rotational axis has n–1 associated operations (excluding $C_n^{\,n} = E$).

Reflection, σ

☞ For every point a distance r along a normal to a mirror plane there exists a point at $-r$.

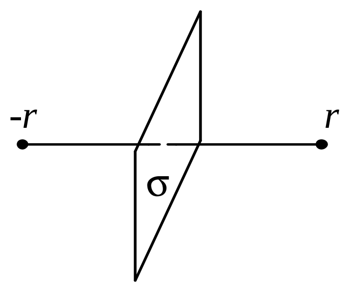


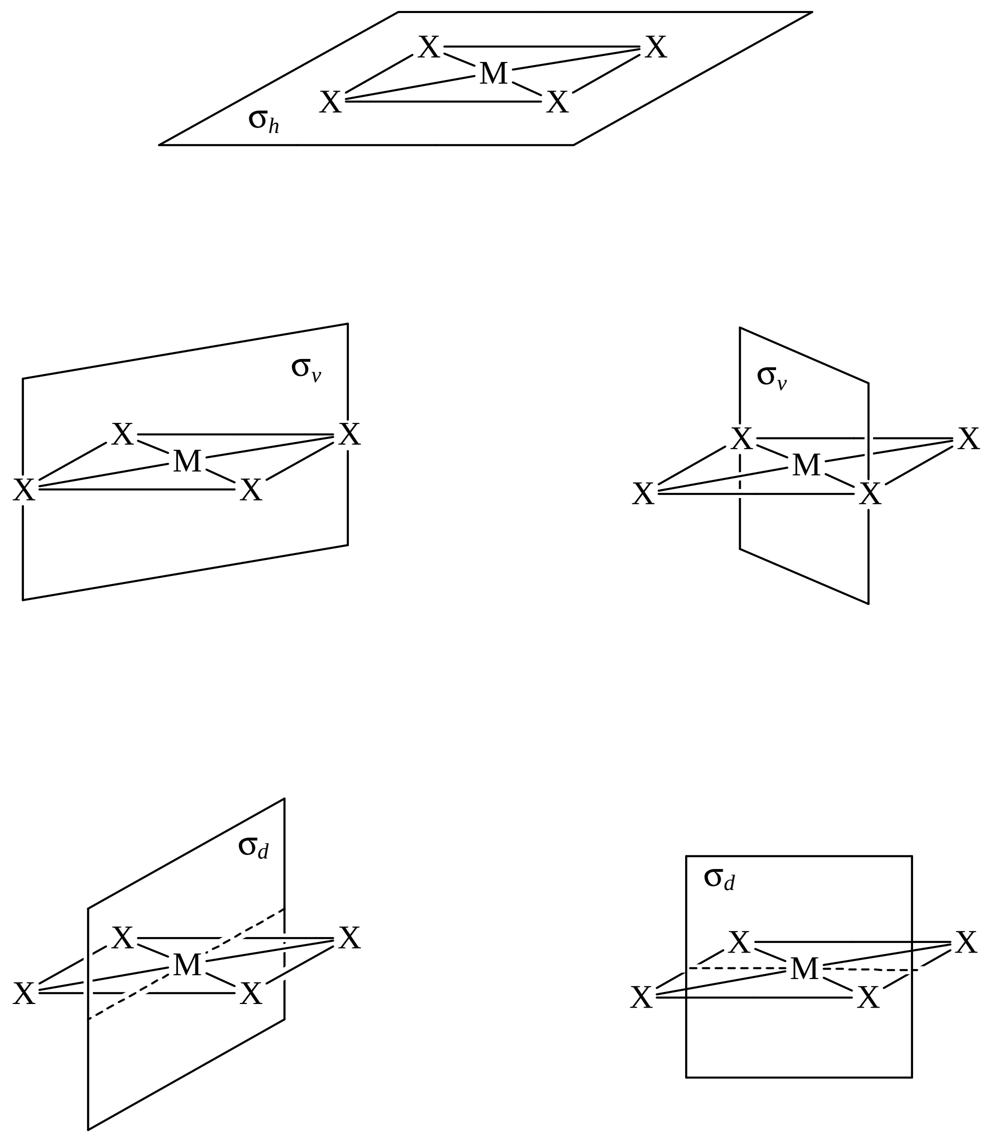
Fig. 1.3 Two points, equidistant from a mirror plane σ, related by reflection.

✓ For a point (x,y,z), reflection across a mirror plane σ_{xy} takes the point into $(x,y,-z)$.

✓ Each mirror plane has only one operation associated with it, since $\sigma^2 = E$.

Horizontal, Vertical, and Dihedral Mirror Planes

Fig. 1.4 Mirror planes of a square planar molecule MX_4.

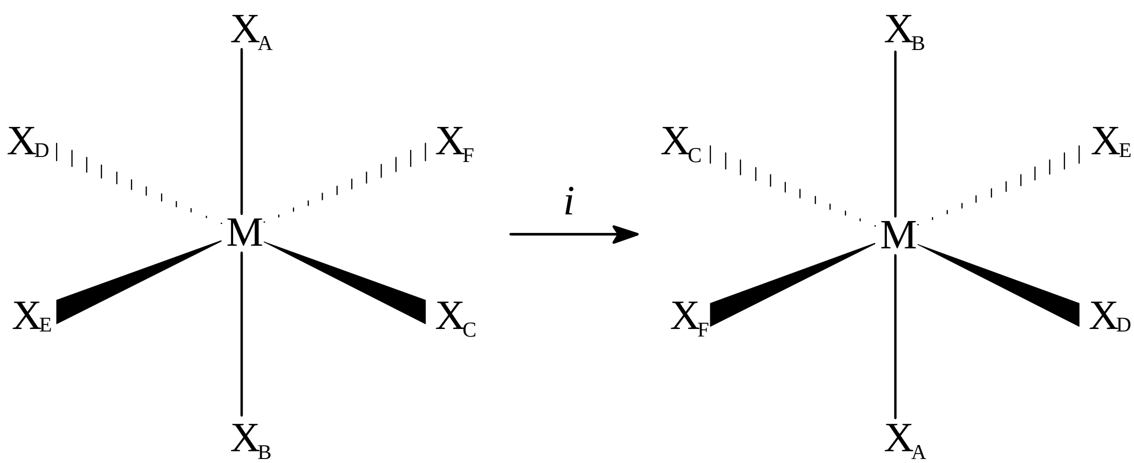


Inversion, *i*

☞ If inversion symmetry exists, for every point (x,y,z) there is an equivalent point $(-x,-y,-z)$.

✓ Each inversion center has only one operation associated with it, since $i^2 = E$.

Fig. 1.6 Effect of inversion (i) on an octahedral MX_6 molecule ($X_A = X_B = X_C = X_D = X_E = X_F$).



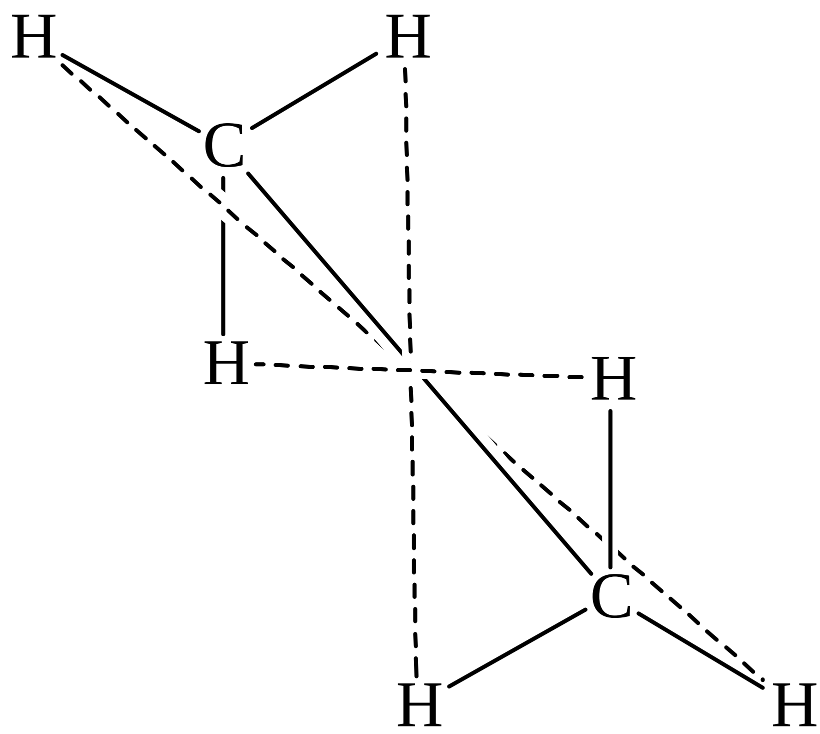


Fig. 1.7 Ethane in the staggered configuration. The inversion center is at the midpoint along the C-C bond. Hydrogen atoms related by inversion are connected by dotted lines, which intersect at the inversion center. The two carbon atoms are also related by inversion.

Rotation-Reflection (Improper Rotation), S_n

☞ S_n exists if the movements C_n followed by σ_h (or vice versa) bring the object to an equivalent position.

✓ If both C_n and σ_h exist, then S_n must exist.

Example: S_4 collinear with C_4 in planar MX_4.

✓ Neither C_n nor σ_h need exist for S_n to exist.

Example: S_4 collinear with C_2 in tetrahedral MX_4.

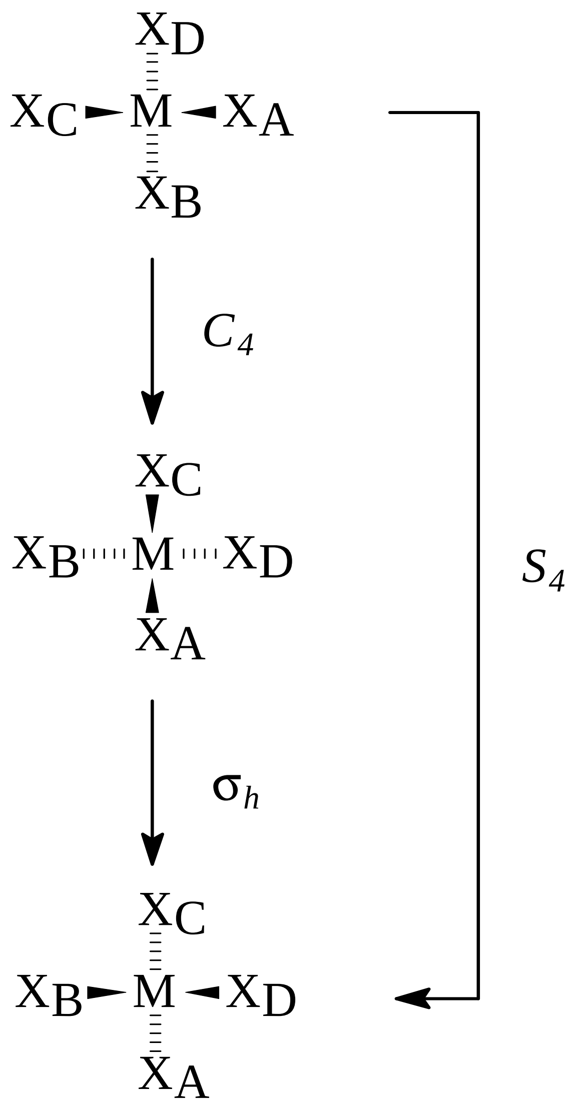


Fig. 1.8 S_4 improper rotation of a tetrahedral MX_4 molecule ($X_A = X_B = X_C = X_D$). The improper axis is perpendicular to the page. Rotation is arbitrarily taken in a clockwise direction. Note that neither C_4 nor σ_h are genuine symmetry operations of tetrahedral MX_4.

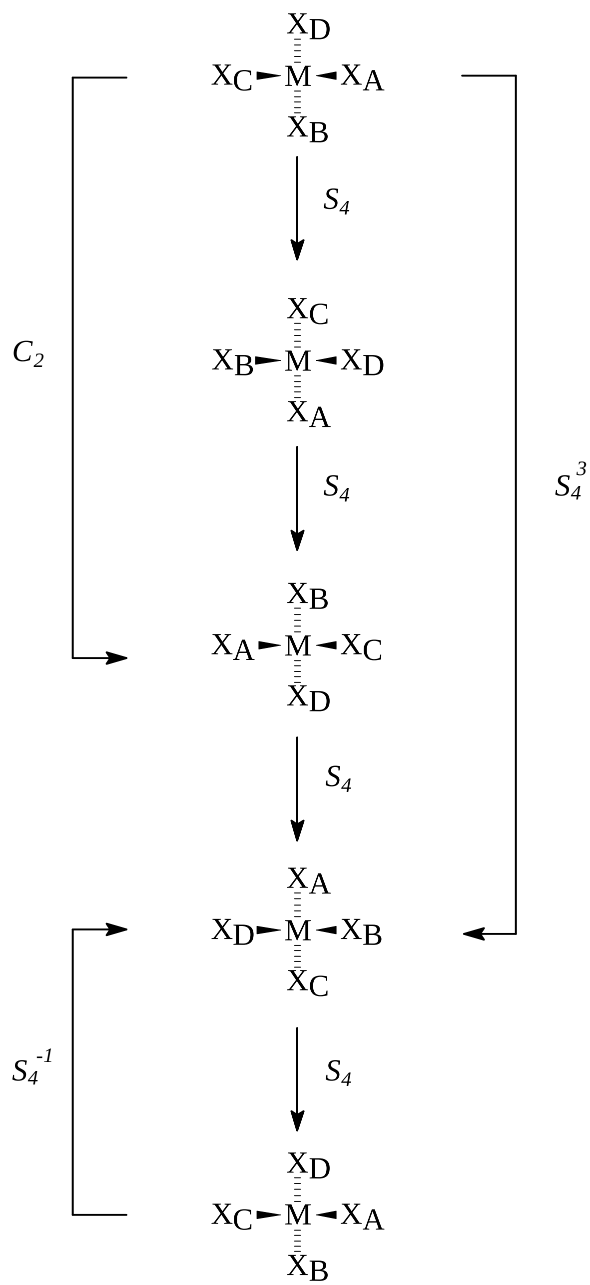


Fig. 1.9 Successive S_4 operations on a tetrahedral MX_4 molecule ($X_A = X_B = X_C = X_D$). Rotations are clockwise, except S_4^{-1}, which is equivalent to the clockwise operation S_4^{3}.

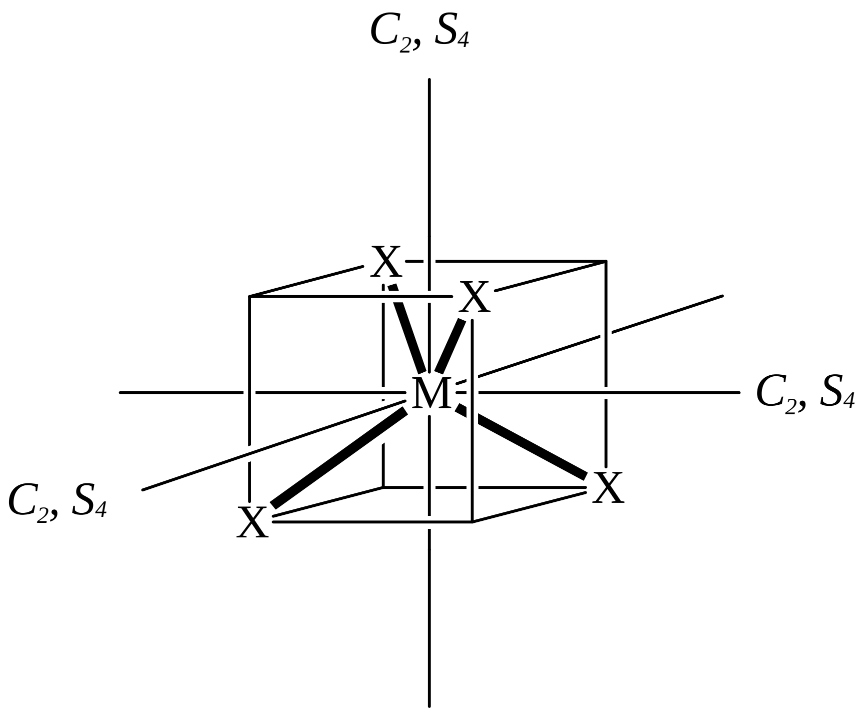


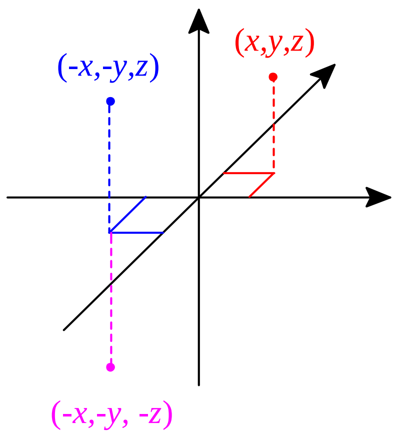
Fig. 1.10 A tetrahedral MX_4 molecule inscribed in a cube. A C_2 axis, collinear with an S_4 axis, passes through the centers of each pair of opposite cube faces and through the center of the molecule.

Non-Genuine S_n Operations:

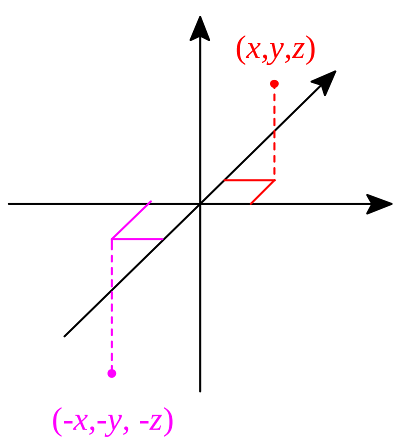
☞ $S_1 = \sigma$

☞ $S_2 = i$

$C_2 + \sigma_h$



i



General Relations of Improper Axes

Equivalences of successive S_n *operations:*

- ✓ If n is even, $S_n^{\ n} = E$
- ✓ If n is odd, $S_n^{\ n} = \sigma$ and $S_n^{\ 2n} = E$
- ✓ If m is even, $S_n^{\ m} = C_n^{\ m}$ when $m < n$ and $S_n^{\ m} = C_n^{\ m-n}$ when $m > n$
- ✓ If S_n with even n exists, then $C_{n/2}$ exists
- ✓ If S_n with odd n exists, then both C_n and σ perpendicular to C_n exist.

Examples

☞ Find all symmetry elements and operations in the following: