INTRODUCTION TO GROUP THEORY

<u>Motivation</u>: The group theory is important in various aspects of our discussion on mesoscopic system. We have actually already made use of it for example when we have assumed the existence of the Bloch theorem for perfect crystals. In particular, nevertheless, the idea behind this introduction is to develop methods that are useful for:

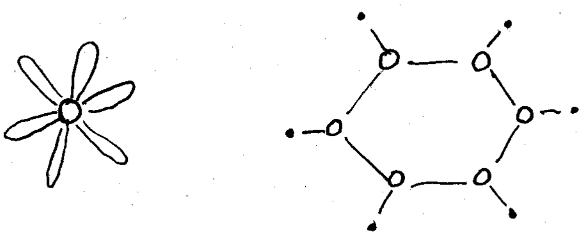
* exact diagonalization of interacting systems
* identification of symmetry protected degenerations

These two points are important in the development of transport theory for molecular transistors that we will analyse later in the course.

Alternatively we could call this section:

"Group theoretical approach for the classification of eigenstates."

<u>BASIC IDEA</u>: The fundamental principle of the group theory is to learn something out of the perception that some properties remain unchanged even if we change our point of view or we operate on the object of our observation. In other words "group theory provides a systematic way of thinking about symmetry".



"H"

Different objects can be studied with group theory

The mathematical concept of group is due to E. Galois (1823)

Def: BINARY COMPOSITION is a law that associates to two abstract elements of a set $g_i\, g_j$ a third element g_k. e.g. Set of square matrices with matrix multiplication. In general the binary composition is called multiplication in group theory.

Def: GROUP is a set of elements and a binary composition with the following properties:

$\boxed{1}$ $A \in \mathcal{G}$ and $B \in \mathcal{G} \Rightarrow A \cdot B \in \mathcal{G}$
$\boxed{2}$ $\exists\ E \in \mathcal{G}: \quad A \cdot E = E \cdot A = A$
$\boxed{3}$ The associative law is valid $(AB)C = A(BC)$
$\boxed{4}$ $\forall A \in \mathcal{G} \quad \exists A^{-1} \in \mathcal{G}: \quad AA^{-1} = A^{-1}A = E$

Notice that $AB = C$ is uniquely defined but in general $AB \neq BA$
If $AB = BA \quad \forall A, B \in \mathcal{G} \Rightarrow$ the group is called Abelian.

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

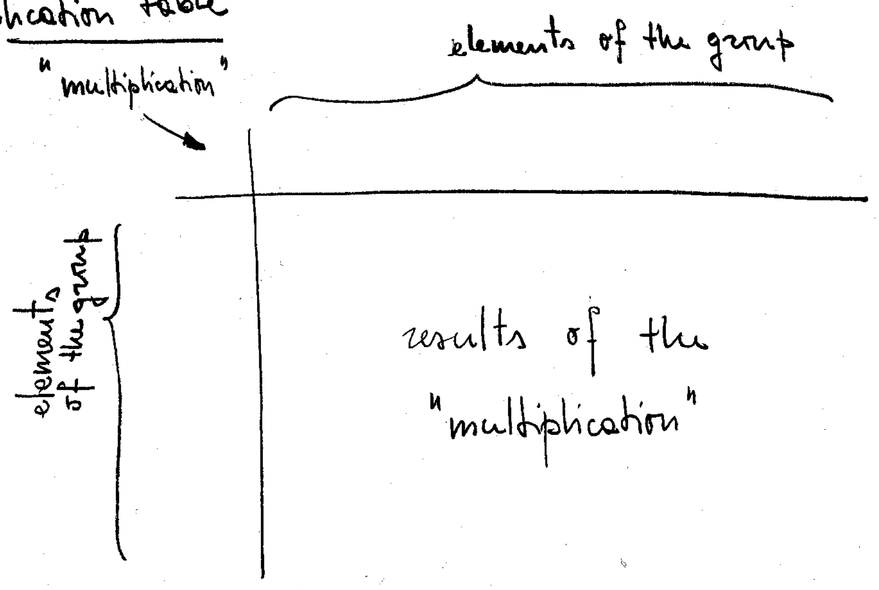
Def: CLASS : a complete set of the elements conjugate to A form the class $\mathcal{C}_A$. The number of elements in the class is called order of the class (in the same way the order of the group).

Def: A mapping(f) of a group $\mathcal{G}$ into $\mathcal{G}'$ is homomorphous if it respects the multiplication:

$$f(AB) = f(A)\, f(B)$$

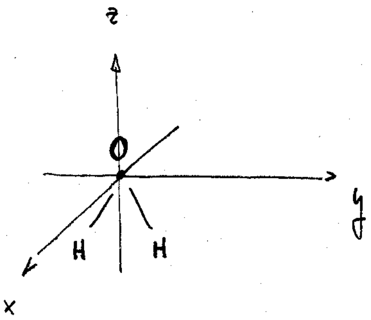
Def: An homomorphous mapping is isomorphous when $\mathcal{G}$ and $\mathcal{G}'$ have the same order and the elements of $\mathcal{G}$ are mapped one-to-one on to the elements of $\mathcal{G}'$.

Multiplication table



Example of multiplication table for the group C_{2v} (see later on for a nomenclature of the groups)

	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



C_2 is a rotation of π around the z axis

$\sigma_{yz,\,xz}$ is a reflection with respect of the plane yz, xz.

The product is "apply the two operations in a ~~row~~, from right to left".

Two isomorphic groups have the same multiplication table. They are a different representation of the same abstract group.

The groups in which we are interested in this context are made 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 that always keep at least one point invariant in the space.

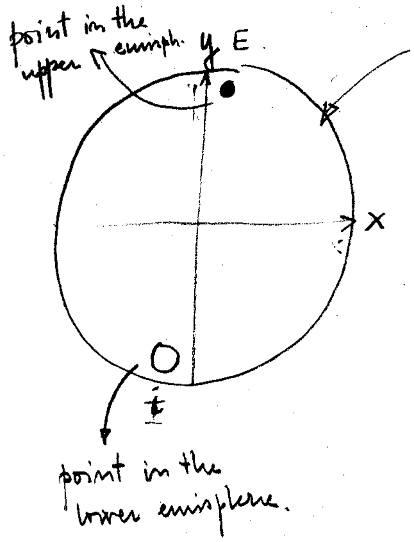
A list:
- E identity (from german Einheit)
- C_n (proper) rotation of $\frac{2\pi}{n}$ radians around a certain axis. The axis with the larger n is called principal axis. If there are twofold axes perpendicular to the principal axis they are called dihedral and denoted C_2' and C_2''.
- S_n Rotation of $\frac{2\pi}{n}$ around a certain axis followed by a reflection with respect to the plane perpendicular to the rotation axis. Also called improper rotation.
- i inversion with respect to a point.
- σ mirror operation (from Spiegel = mirror) with respect to a plane

  σ_h perpendicular to the main rotation axis
  σ_v containing the main rotation axis
  σ_d special case of σ_v but with the plane bisecting the angle between 2 dihedral axes.

Def: SYMMETRY ELEMENT is a point, a line or plane with respect of which a point symmetry operation is carried out. The notation given above is in reality the Schönflies for symmetry elements.

Def: A <u>POINT GROUP</u> is a group whose elements are POINT symmetry operations.

Projection diagrams are useful representations of point groups



projection of a sphere of unity radius in the xy plane

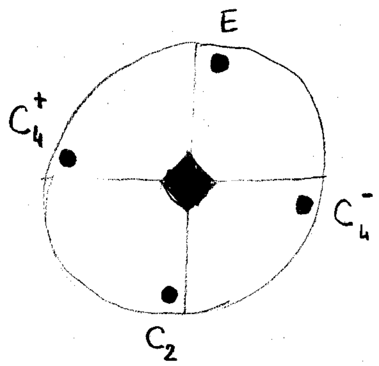
The order of the main rotation axis is given by dark "polygon" in the center

PROPER GROUPS

i $\boxed{\text{Cyclic groups}}$ C_n there is only 1 axis of rotation and the group elements are E, $C_{n[z]}^{(\pm k)}$

example

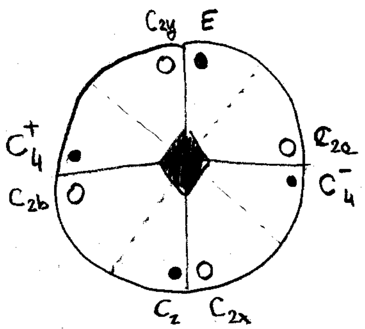
C_4



ii $\boxed{\text{Dihedral groups}}$ Proper rotations that transform a regular n-sided prism into itself. The symmetry elements are C_n and $n\,C_2'$. The symbol D_n

example

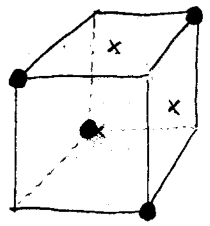
D_4



$a = \frac{1}{\sqrt{2}}\,[1\,1\,0]$

$b = \frac{1}{\sqrt{2}}\,[\bar{1}\,1\,0]$

iii $\boxed{\text{Tetrahedral group}}$ proper rotations that transform a tetrahedron into itself. Called T. The symmetry elements are $3C_2$ and $4C_3$



iv $\boxed{\text{Octahedral or cubic group}}$ called O. proper rotations that transform a cube or an octahedron into itself.

The symmetry elements $3C_4$ $4C_3$ $9C_2$

v $\boxed{\text{Icosahedral group}}$ called Y. Consists of the proper rotations that transform an icosahedron or pentagonal dodecahedron into itself.

$$Y = \{E \quad 6C_5^{\pm} \quad 10C_3^{\pm} \quad 15C_2\}$$

IMPROPER GROUPS

It is useful for the most compact definition of the improper groups to introduce the definition of outer direct product.

$A = \{a_i\}$ group of order a $\qquad A \otimes B = G = \{g_k\} \quad g_k = (a_i, b_j)$

$B = \{b_j\}$ group of order b

$(a_i, b_j)(a_\ell, b_m) = (a_i a_\ell, b_j b_m) = (a_p, b_q)$ due to closure of A and B.

If $(a_i, b_j) = a_i b_j$ (same product definition in A and B

$\Rightarrow$ ① $a_\ell b_j = b_j a_\ell \quad \forall\ \ell, j$

② $A \cap B = E$

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

$C_i = \{E, i\}$

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

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

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.

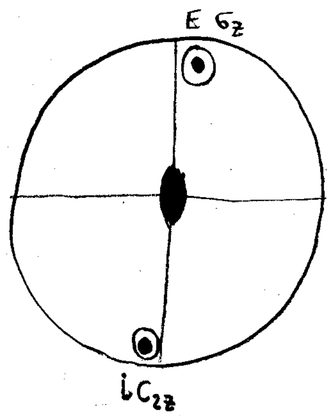
— if n is even $D_n \otimes C_i = D_{nh}$

iii) $T \otimes C_i = T_h$

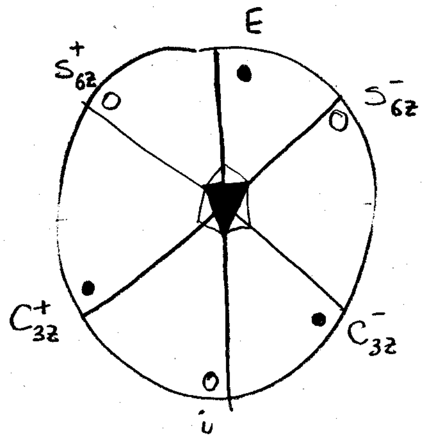
iv) $O \otimes C_i = O_h$

v) $Y \otimes C_i = Y_h$

<u>Example</u>



C_{2h}



S_6

IDENTIFICATION OF MOLECULAR POINT GROUPS

Linear molecules
- no σ_h → $C_{\infty v}$ (Hydrogen chloride H - Cl)
- σ_h → $D_{\infty h}$ (Carbon dioxide O = C = O)

Non-linear molecules

- no proper axis of symmetry
  - σ — C_s
  - i — C_i
  - neither σ nor i — C_1
- C_n, $n > 1$
  - $\leqslant 1\, C_3$
    - $n C_2' \perp C_n$
      - σ_h — D_{nh} ⇝ 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 — S_{2n}
      - no σ, no i — C_n
  - $> 1\, C_3$
    - $10\, C_3, 6\, C_5$
      - i — I_h
      - no i — I
    - $4\, C_3$
      - $3 S_4$ — T_d ⇝ Methane
      - $3 C_4$
        - i — O_h
        - no i — O
      - $3 C_2$
        - i — T_h
        - no i — T

MATRIX REPRESENTATIVES

Def: A vectorial space on $\mathbb{R}$ (or $\mathbb{C}$) is a set V on which we have consistently defined 2 operation

- sum : $v_1, v_2 \in V \Rightarrow v_1 + v_2 = v_3$
- product with a scalar $a \in \mathbb{R}$ (or $\mathbb{C}$) $a v_1$

the operation must satisfy the following properties

V is an Abelian group with respect to +

$$\begin{cases} \forall u\ v\ w \in V & (u+v)+w = u+(v+w) \\ \exists\, 0 \in V : \forall v \in V & v + 0 = 0 + v = v \\ \forall v \in V\ \exists -v \in V : & v + (-v) = (-v) + v = 0 \\ \forall v, w \in V & v + w = w + v \end{cases}$$

$$\forall \lambda \in \mathbb{R}\ (\text{or } \mathbb{C})\ \forall v, w \in V \quad \lambda(v+w) = \lambda v + \lambda w$$

$$\forall \lambda, \mu \in \mathbb{R}\ (\text{or } \mathbb{C})\ \forall v \in V \quad (\lambda + \mu) v = \lambda v + \mu v$$

$$\forall \lambda, \mu \in \mathbb{R}\ (\text{or } \mathbb{C})\ \forall v \in V \quad (\lambda \mu) v = \lambda(\mu v)$$

$$\forall v \in V \quad 1 v = v \quad \text{and} \quad 0 v = 0$$

Notice that $\mathbb{R}$ or $\mathbb{C}$ can be substituted with whatever other field $\mathbb{K}$.

Def: An application $f: V \to V$ is linear if:

$$f(\alpha v + \beta w) = \alpha f(v) + \beta f(w) \quad \forall v, w \in V \quad \alpha, \beta \in \mathbb{K}.$$

In particular the following theorem holds. The space of linear transformations $V \to V$ is isomorphous to the space of matrices $n \times n$ with entries taken from $\mathbb{K}$.

$$\mathrm{Hom}_{\mathbb{K}}(V_n, W_m) \simeq \mathrm{Mat}(m, n; \mathbb{K})$$

Our point symmetry operations are all linear operations acting first of all on the points of $\mathbb{R}^3$ which is a vectorial space on $\mathbb{R}$.

$f: \mathbb{R}^3 \to \mathbb{R}^3$. In order to find the corresponding real 3×3 matrix is enough to take a basis for $\mathbb{R}^3$ and apply f to each of the element of the basis and decompose the result on the same basis.

$\mathbb{R}^3 \to \quad \hat{e}_x \; \hat{e}_y \; \hat{e}_z$

$$f(\hat{e}_x) = \hat{v}_x = a\hat{e}_x + b\hat{e}_y + c\hat{e}_z$$
$$f(\hat{e}_y) = \hat{v}_y = d\hat{e}_x + e\hat{e}_y + f\hat{e}_z$$
$$f(\hat{e}_z) = \hat{v}_z = g\hat{e}_x + h\hat{e}_y + i\hat{e}_z$$

$$f(\hat{v}) = \hat{W} = \alpha'\hat{e}_x + \beta'\hat{e}_y + \gamma'\hat{e}_z$$
$$\parallel$$
$$f(\alpha\hat{e}_x + \beta\hat{e}_y + \gamma\hat{e}_z) = \alpha\hat{v}_x + \beta\hat{v}_y + \gamma\hat{v}_z = (\alpha a + \beta d + \gamma g)\hat{e}_x + (\alpha b + \beta e + \gamma h)\hat{e}_y + (\alpha c + \beta f + \gamma i)\hat{e}_z$$

written in components: $$\begin{pmatrix}\alpha'\\ \beta'\\ \gamma'\end{pmatrix} = \begin{pmatrix} a & d & g\\ b & e & h\\ c & f & i\end{pmatrix}\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix}.$$

All the point symmetry operations that we consider preserve the scalar prod. defined on $\mathbb{R}^3$ $\quad (v, w) = (f(v), f(w))$