Symmetry

SS 2002: Profs. Engelen and Schwarz
Mittwochs, 8:22-10 h, AR-G113
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Übungs-Abgabe Montag abends, Briefkasten AR-K602

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Part II: Periodic Systems (Engelen)

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1 Symmetry Groups

1.1 Groups

Def: A Group is a set of different elements, and a combination (Verknüpfung) $\circ$ or $\cdot$ (so-called group multiplication), with fulfills 4 axioms:
1) closed, $a \cdot b = c$;
2) associative, $(a \cdot b) \cdot c = a \cdot (b \cdot c)$, so one can write $a \cdot b \cdot c$;
3) there is just one neutral or unit element $e, a \cdot e = e \cdot a = a$;
4) every element a has its inverse, $a^{-1} = b$, with $a \cdot b = b \cdot a = e$. Note: $e^{-1} = e$; law: $(a \cdot b)^{-1} = b^{-1} \cdot a^{-1}$!
In general (i.e. in some cases) $a \cdot b \neq b \cdot a$, the elements do not commute in every case, the commutator does not always vanish: $[a, b] = ab - ba \neq 0$.
However for specific groups, $ab = ba$ always for any a, b : these groups are called abelian (abelsch) or commutative.
Examples of abelian groups:
$\{$all vectors $|a\rangle\}$ and "addition"; e is the zero vector $|0\rangle$; inverse of $|a\rangle$ is $-|a\rangle$.
$\{$all numbers $\neq 0\}$ and "multiplication"; e is 1; the inverse of a is $1/a$.
Examples of nonabelian groups:
$\{$function operators$\}$ and applying them one after the other; e is $1\cdot$; the inverse of $x\cdot$ is $1/x\cdot$; of d/dx it is $\int dx$; of $\sqrt{()}$ it is $()^2$, etc.;
note: $[x\cdot, d/dx] = x \cdot d/dx - d/dx \cdot x\cdot = 1\cdot$!!
$\{$geometric identity operations$\}$ and applying one after the other; e is "no change"; the inverse is "reverse the change";
note: for an equilateral triangle in the plane we have 6 elements, the order of the group is 6: $E, C_3, C_3^2 = C_3^{-1}, \sigma^I, \sigma^{II}, \sigma^{III}$ with $C_3\sigma^I = \sigma^{III}$ and $\sigma^I C_3 = \sigma^{II}$. $\sigma^{-1} = \sigma$.
Equivalence: C_3 and C_3^{-1} are different, but very similar. Concerning the symmetric triangle (though not the wind meter), C_3 and C_3^{-1} are equivalent. The following mathematical defintion of equivalence is in agreement with the above mentioned intuitive concept: a and b are equivalent, $a \wedge b$, if there is a c with $a = c^{-1}bc$ or $ca = bc$.
The equivalence relation is reflexive, $a \wedge a$; it is symmetric: if $a \wedge b$ also $b \wedge a$; it is transitive: if $a \wedge b$ and $b \wedge c$, then also $a \wedge c$.
Therefore a group consists of nonoverlapping equivalence classes. e forms always a class for itself. In abelian groups obviously every element forms a separate class.
Example: the symmetry group of the equilateral triangle in two dimensions has three classes: $(E), (C_3, C_3^{-1}), (\sigma^I, \sigma^{II}, \sigma^{III})$ or $(E, 2C_3, 3\sigma)$.

1.2 Symmetry

In science a physical object (e.g. molecule, crystal) is described by a mathematical formula $\mathcal{F}$: In the case of rigid bodies (nonvibrating molecules and crystals) by the coordinates; in the case of flexible systems (electrons, vibrating or rearranging nuclei) by the equation of motion.
If we change the coordinates x to x' by a coordinate transformation $T_{x \to x'}$, then the description formula $\mathcal{F}(x)$ changes into another formula $\mathcal{F}'(x')$. For specific transformations S the transformed formula has the same form as the original formula:

$$\mathcal{F}(x) \xrightarrow{S_{x \to x'}} \mathcal{F}'(x') = \mathcal{F}(x')$$

Example: For the rotation of the plane
$x = x' \cdot \cos\phi + y' \cdot \sin\phi; y = y' \cdot \cos\phi - x' \cdot \sin\phi$, i.e. $\vec{x} = C^{\phi} \cdot \vec{x}'$,
the expression of the Coulomb force $\mathcal{F}(x) = 1/(x^2 + y^2)$ is transformed to $\mathcal{F}'(x') = 1/(x'^2 + y'^2) = \mathcal{F}(x')$. The Coulomb force is form-invariant against rotations, it has "rotational symmetry". S is then called a symmetry transformation. All symmetries, which let the description formula of the object form invariant, form a group: the symmetry group of the object.

Common symmetries (coordinate transformations) of objects are: Rotations, reflections, inversions, translations of the spatial and/or time coordinates; permutations of the numbering of the coordinates of identical particles (electrons, same isotopic nuclei).
Note: two classical objects are never identical, this phenomenon does not occur in daily life, only in the microscopic world.
Note: Instead of transforming the reference coordinates ("turn your head, look through a mirror") it is sometimes easier to visualize if one transforms the object ("rotate or invert the molecule"), although many molecules cannot be inverted without bond breaking!

1.3 Symmetries of rigid bodies

If the nuclei in molecules or crystal unit cells do not undergo large amplitude motions or structural rearrangements, the system may approximately be modeled by a rigid body. The symmetry transformations keep at least the central point of the system unchanged. These symmetry groups are called point groups.

Symmetry transformations of rigid bodies are:
n-fold rotations $C_n : (C_n)^n = E, (C_n)^{n-1} = C_n^{-1}$
mirror reflection (Spiegelung) $\sigma : \sigma^2 = E, \sigma^{-1} = \sigma$
rotational reflection (Drehspiegelung) $S_n = C_n \cdot \sigma_h = \sigma_h \cdot C_n$:
$S_1 = \sigma = I_2; S_2 = i = I_1$ (inversion); $S_3 = I_6^{-1}; S_3^6 = E; S_4 = I_4^{-1}$
I_n (rotational inversion, Drehinversion) $= C_n \cdot i = i \cdot C_n$
Schoenflies uses the symbols $C_n, \sigma_v, \sigma_h, S_n$
Hermann and Mauguin use $n, m, /m$, but $\bar{n} = I_n$!

Point groups (example molecules in parentheses):

asymmetric	C_1
only a mirror plane	C_s
only an inversion center	C_i
only a symmetry axis	$C_n (n = 2, 3, ...)$
vertical C_n and horizontal σ, also S_n	C_{nh}
vertical C_n and vertical σ's (if n even, σ_v and σ_d):	C_{nv}
S_{2n} but no C_{2n} (but C_n)	S_{2n}
C_n and C_2 at 90°	D_n
C_n and $C_2\perp$ and σ_h (and S_n and σ_v)	D_{nh}
C_n and $C_2\perp$ and vertical σ_d and S_n but no σ_h	D_{nd}
"linear"(cylindrical)	$C_{\infty v}, D_{\infty h}$
Platonic bodies (equilateral surfaces)	
3 triangles at each corner	Tetrahedron – T, T_h, T_d
4 triangles at each corner	Octahedron – O, O_h
5 triangles at each corner	Ikosaeder – I, I_h
3 squares at each corner	Hexaeder or cube – O_h (!)
3 pentagons at each corner	Dodekaeder – I_h (!)
sphere	– O_3

Note the conceptual differences between the symmetry operation (group element) C_n-rotation, the equivalent class $C_n = (C_n, C_n^{-1})$, the symmetry element C_n-axis, the symmetry group C_n. A symmetry element is not an element of the symmetry group.

Chirality: a molecule is "handy" if, even after rotation, it does not coincide with its mirror or inversion image. Then it will interact differently with left/right polarized light or with left/right isomeric molecules. A chiral molecule or unit cell does not posses any S_n or I_n. Systems with symmetry group C_n or D_n may be chiral. Symmetric carbon atoms or asymmetric atoms are neither necessary nor suffiecient for chirality.
nonchiral: Mesoweinsäure, HNRAr
chiral: Alanin, Weinsäure, HPRAr, HRCCCRH, $[Fe(Ox)_3]^{3-}$, Helicen

Crystal classes
Those point groups, which can occur for crystal unit cells: only those with C_1, C_2, C_3, C_4, C_6 axes. There are only 32 three-dimensional crystal classes: C_1, C_i (2 triclinic); C_s, C_2, C_{2h} (3 monoclinic); C_{2v}, D_2, D_{2h} (3 (ortho-)rhombic); C_4, S_4, C_{4h}, C_{4v}, D_{2d}, D_4, D_{4h} (7 tetragonal); C_3, C_6, S_6, C_{3h}, C_{6h}, C_{3v}, C_{6v}, D_3, D_6, D_{3d}, D_{3h}, D_{6h} (12 trigonal/hexagonal/rhombohedral); T, T_h, T_d, O, O_h (5 cubic).

There are also groups for "one-dimensional materials", for two-dimensional surfaces, for quasi- and liquid crystals, for flexible molecules (e.g. ethan, bullvalen).
Note the conceptual difference between crystal class (a group) and equivalence class (a set of similar group elements).
Note: other axes can also occur for quasicrystals.