
Symmetry

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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: $[x \cdot, d/dx] = x \cdot d/dx - d/dx \cdot x \cdot = \underline{1}$. !!

{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 group 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 definition 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 $T_{x \rightarrow x'}$, 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:

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

Example: For the rotation of the plane

$$x = x' \cdot \cos \phi + y' \cdot \sin \phi; y = y' \cdot \cos \phi - x' \cdot \sin \phi, \text{ i.e. } \vec{x} = C^\phi \cdot \vec{x}'$$

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) $S_n = C_n \cdot \sigma_h = \sigma_h \cdot C_n$:

$$S_1 = \sigma = I_2; S_2 = i = I_1 \text{ (inversion); } S_3 = I_6^{-1}; S_3^6 = E; S_4 = I_4^{-1}$$

$$I_n \text{ (rotational inversion, Drehinversion) } = C_n \cdot i = i \cdot C_n$$

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 (Et-FCl)
only a mirror plane	C_s (NOCl)
only an inversion center	C_i ((CHBrCl) ₂)
only a symmetry axis	C_n ($n = 2, 3, \dots$) (rigid H ₂ O ₂)
vertical C_n and horizontal σ , also S_n	C_{nh} (CHCl) ₂
vertical C_n and vertical σ 's (if n even, σ_v and σ_d):	C_{nv} (H ₂ O, PH ₃)
S_{2n} but no C_{2n} (but C_n)	S_{2n} (C ₈ H ₄ Cl ₄)
C_n and C_2 at 90°	D_n (MO _x 3)
C_n and $C_2 \perp$ and σ_h (and S_n and σ_v)	D_{nh} (C ₆ H ₆)
C_n and $C_2 \perp$ and vertical σ_d and S_n but no σ_h	D_{nd} (H ₂ C ₃ H ₂)
"linear" (cylindrical)	$C_{\infty v}, D_{\infty h}$ (HCl, N ₂)
Platonic bodies (equilateral surfaces)	
3 triangles at each corner	Tetrahedron – T, T_h, T_d (CH ₄)
4 triangles at each corner	Octahedron – O, O_h (ML ₆)
5 triangles at each corner	Ikosaeder – I, I_h (B ₁₂ H ₁₂)
3 squares at each corner	Hexaeder or cube – O_h (!) (C ₈ H ₈)
3 pentagons at each corner	Dodekaeder – I_h (!) N ₂₀
sphere	– O_3 (Ar)

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 possess any S_n or I_n . Systems with symmetry group C_n or D_n may be chiral. Asymmetric carbon atoms or asymmetric atoms are neither necessary nor sufficient 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, are 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.

2 Matrix Representations

2.1 Vectors, Operations, Matrices

See section 10 of Physikalische and Theoretische Chemie I. Nuclear positions and motions are described in the classical approximation by 3-dimensional Euklidian vectors $\vec{f}(t)$; and nuclei and electrons at the quantum level by wave functions (= state vectors $\vec{f}(x, t)$ in ∞ -dimensional Hilbert space). The natural laws for stationary states \vec{g} can be formulated most generally as $\mathcal{H}(x) \circ \vec{g}_n(x) = 0$, where \vec{g}_{nm} ($m = 1$ to d_n), the respective energy or frequency λ_n are the eigen-solutions.

If \mathcal{S} is a symmetry operation of the description formula of the system, $\mathcal{S}^{-1} = \mathcal{H}\mathcal{S} = \mathcal{H}$, i.e., \mathcal{H} is invariant under \mathcal{S} , then it follows, from $\mathcal{H}\vec{g} = 0$ that $\mathcal{H}\mathcal{S}\mathcal{S}^{-1}\vec{g} = 0 \rightarrow (\mathcal{S}^{-1}\mathcal{H}\mathcal{S})(\mathcal{S}^{-1}\vec{g}) = 0 \rightarrow \mathcal{H}(\mathcal{S}\vec{g}) = 0$

A symmetry transformed state vector is an equivalent vector, any $\mathcal{S}\vec{g}_{nm}$ is also an eigen-solution with the same λ_n as \vec{g}_{nm} .

Example: The atomic nuclear Coulomb potential is rotationally symmetric. Therefore the states of atoms are transformed by rotations into states of the same energy. A rotated p-orbital is also one of the p-state-manifold.

If \vec{g}_n is nondegenerate and real, the state vector is either symmetric: $\mathcal{S}\vec{g}_n = \vec{g}_n \cdot +1$, or it is antisymmetric: $\mathcal{S}\vec{g}_n = \vec{g}_n \cdot -1$. In the case of degenerate state vectors \vec{g}_{nm} $\mathcal{S}\vec{g}_{nm} = \sum_i \vec{g}_{ni} \cdot D_{im}$. D_{im} is a matrix representation matrix of \mathcal{S} . In the nondegenerate case, D is a 1×1 -matrix.

If \vec{g}_{nm} is an orthonormal set of d_n degenerate eigenvectors, then any complete orthonormal linear combination set of them is an equivalent set. The values of the representation matrix elements D_{nm} are changed, but the trace (Spur) $\sum_i D_{ii} = \chi_n$ is unchanged. χ_n is characteristic for the set of eigenvectors \vec{g}_{nm} corresponding to λ_n .

The symmetry of the eigensolutions to λ_n is uniquely specified by the $\chi_n(\mathcal{S})$, where the \mathcal{S} are the g different symmetry operations of the symmetry group. $\vec{\chi}$ is the g -dimensional character vector. The symmetry species (Rasse is named by a (lower or upper case) letter, see the table.

2.2 Irreducible Representations

There are just as many different symmetry types (or irreducible representations) Γ as there are different classes of the group, no more. There is always the unit class (E), and the totally symmetric, one-dimensional species $\vec{\chi} = (1, 1, \dots, 1)$. The dimensions of species

Γ are $\chi^\Gamma(E)$, these are the possible degeneracies of energies and frequencies of the system. The symmetry group determines the degeneracy pattern of stationary states. Since equivalent \mathcal{S} have the same character, only the "contracted" character vectors are given in the group tables. The character vectors $\vec{\chi}$ of different species a, b are orthonormal:

$$\langle \chi^a | \chi^b \rangle = \sum_s \chi^a(\mathcal{S})^* \cdot \chi^b(\mathcal{S}) = \sum_k \chi^a(\mathcal{K})^* \cdot \chi^b(\mathcal{K}) \cdot n_k = g \cdot \delta_{ab} \quad (2.1)$$

where n_k is the number of equivalent symmetry operations in equivalence class \mathcal{K} , and $\delta_{ab} = 1$ for $a = b$ and 0 for $a \neq b$. Given several states with their $d_1 + d_2 + \dots = d$ state function, or given a set of basis functions describing several states $1, 2, \dots$, the the representation matrices are $d \times d$ -dimensional, and the character vector is $\vec{\chi} = \vec{\chi}^1 + \vec{\chi}^2 + \dots$. "The reducible matrix representation consists of several irreducible components". Sometimes the same species γ occurs several (n_γ) times:

$$\vec{\chi} = \sum_\gamma \vec{\chi}^\gamma \cdot n_\gamma \quad (2.2)$$

From equations 2.1 and 2.2 follows

$$n_\gamma = \langle \chi^\gamma | \chi \rangle / g = 1/g \cdot \sum_k \chi^\gamma(\mathcal{K}) \cdot \chi(\mathcal{K}) \cdot n_k \quad (2.3)$$

With this important formula we can determine, which types and numbers of eigenstates exist in electronic (orbitals, state function) and nuclear systems (normal vibrations).

Example: Given a system with C_{3v} symmetry (e.g. PH_3), the group consists of (E), (C_3, C_3^2) = $2C_3$, ($\sigma'_v, \sigma''_v, \sigma'''_v$) = $3\sigma_v$. As basis we choose the z-shifts of the 4 nuclei, or 4-atomic s-valence orbitals. The 4×4 -matrix representation of the symmetry group operators is:

$$D : \begin{array}{c|ccc|ccc|ccc|ccc|ccc|ccc} & \mathbf{E} & & & \mathbf{C}_3 & & & \mathbf{C}_3^2 & & & \sigma'_v & & & \sigma''_v & & & \sigma'''_v & & & \\ \hline & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & \\ \hline & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & \\ \hline & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & \\ \hline & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & \end{array}$$

$$\chi : \quad 4 \quad \quad 1 \quad \quad 1 \quad \quad 2 \quad \quad 2 \quad \quad 2$$

Short version of the character vector: $\vec{\chi} = (4, 1, 2)$. We transform to the "symmetry

adapted" basis with the help of the transformation matrix $T = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{3} & 0 & 2/\sqrt{6} \\ 0 & 1/\sqrt{3} & 1/\sqrt{2} & -1/\sqrt{6} \\ 0 & 1/\sqrt{3} & -1/\sqrt{2} & -1/\sqrt{6} \end{pmatrix}$.

The transformed matrix representation is

$$D^T : \begin{array}{c|ccc|ccc|ccc|ccc|ccc|ccc} \hline & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & \\ \hline & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & \\ \hline & 0 & 0 & 1 & 0 & 0 & 0 & -1/2 & +\sqrt{3}/2 & 0 & 0 & -1/2 & -\sqrt{3}/2 & 0 & 0 & 1/2 & \sqrt{3}/2 & 0 & 0 & -1/2 & -\sqrt{3}/2 & \\ \hline & 0 & 0 & 0 & 1 & 0 & 0 & -\sqrt{3}/2 & -1/2 & 0 & 0 & \sqrt{3}/2 & -1/2 & 0 & 0 & -\sqrt{3}/2 & -1/2 & 0 & 0 & -\sqrt{3}/2 & 1/2 & \end{array}$$

$$\chi : \quad 4=1+1+2 \quad \quad 1=1+1-1 \quad \quad 1=1+1-1 \quad \quad 2=1+1+0 \quad \quad 2=1+1+0 \quad \quad 2=1+1+0$$

With the above given transformation trick, we have "reduced" the 4-dimensional reducible representation into its irreducible components: $\chi = A_1 + A_1 + E = 2A_1 + E$

Applying eq. (2.3) we obtain (Note: the n_γ must be 0,1,2,...):

C_{3v}	$1 \cdot E$	$2 \cdot C_3$	$3 \cdot \sigma_v$	$g=6$
A_1	1	1	1	
A_2	1	1	-1	
E	2	-1	0	
χ	4	1	2	$2A_1 + E$

A_1	$1 \cdot 4$	$+1 \cdot 2 \cdot 1$	$+1 \cdot 3 \cdot 2$	$12/6=2$
A_2	$1 \cdot 4$	$+1 \cdot 2 \cdot 1$	$-1 \cdot 3 \cdot 2$	0
E	$2 \cdot 4$	$-1 \cdot 2 \cdot 1$	$+0 \cdot 3 \cdot 2$	$6/6=1$

2.3 Group Character Tables

Point Symmetry Group:

Schoenflies-symbol

Hermann-Mauguin-symbol

Equivalence Classes of symmetry operations

Irreducible Representations = Species = Rasse

A, Σ, S - one-dimensional, +1 for C_n

B - one-dimensional, -1 for C_n

$E, \Pi, \Delta, \Phi, \dots$ - two-dimensional

T, P - three-dimensional

G - four-dimensional

H, D - five-dimensional

g, u - gerade/ungerade for i (!!)

1, 2 - +1 or -1 for σ_v (not unique, if σ_v and σ_d)

Character = sum of values (trace) concerning a symmetry transformation (of a given class) of degenerate eigenvectors into itself.

Examples for the species: translation or dipole operators; rotation operators; quadruple operators.

$D_{nd} (n = 2, 3)$

$D_{2d} = V_d$ ($\bar{4}2m$)	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	$x^2 - y^2$
B_1	1	-1	1	1	-1	z	xy
B_2	1	-1	1	-1	1	(x, y)	(xz, yz)
E	2	0	-2	0	0	(R_x, R_y)	

D_{3d} ($\bar{3}m$)	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$	
A_{1g}	1	1	1	1	1	1	$x^2 + y^2, z^2$
A_{2g}	1	1	-1	1	1	-1	R_z
E_g	2	-1	0	2	-1	0	(R_x, R_y)
							$(x^2 - y^2, xy)$
							(xz, yz)
A_{1u}	1	1	1	-1	-1	-1	
A_{2u}	1	1	-1	-1	-1	1	z
E_u	2	-1	0	-2	1	0	(x, y)

C_{nv} ($n = 2, 3, 4, 5, 6, \infty$)

C_{2v} ($2mm$)	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

C_{3v} ($3m$)	E	$2C_3$	$3\sigma_v$			
A_1	1	1	1	z		$x^2 + y^2, z^2$
A_2	1	1	-1	R_z		
E	2	-1	0	$(x, y)(R_x, R_y)$		$(x^2 - y^2, xy)(xz, yz)$

C_{4v} ($4mm$)	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$		
A_1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	R_z	
E_1	2	$2 \cos 72^\circ$	$2 \cos 144^\circ$	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	$2 \cos 144^\circ$	$2 \cos 72^\circ$	0		$(x^2 - y^2, xy)$

C_{6v} ($6mm$)	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$		
A_1	1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	-1		
B_2	1	-1	1	-1	-1	1		
E_1	2	1	-1	-2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$

$C_{\infty v}$	E	$2C_\infty^\phi$	\dots	$\infty\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	\dots	1	z	$x^2 + y^2, z^2$
$A_2 \equiv \Sigma^-$	1	1	\dots	-1	R_z	
$E_1 \equiv \Pi$	2	$2 \cos \phi$	\dots	0	$(x, y)(R_x, R_y)$	(xz, yz)
$E_2 \equiv \Delta$	2	$2 \cos 2\phi$	\dots	0		$(x^2 - y^2, xy)$
$E_3 \equiv \Phi$	2	$2 \cos 3\phi$	\dots	0		
\dots	\dots	\dots	\dots	\dots		

$C_{nh} (n = 2, 3, 4)$

C_{2h} ($2/m$)	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

C_{3h} ($\bar{6}$)	E	C_3	C_3^2	σ_h	S_3	S_3^5		$\epsilon = \exp(2\pi i/3)$
A'	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
E'	$\begin{pmatrix} 1 & \epsilon & \epsilon^2 \\ 1 & \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon & \epsilon^2 \\ \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon^2 & \epsilon \\ \epsilon & \epsilon^2 \end{pmatrix}$	1	$\begin{pmatrix} \epsilon & \epsilon^2 \\ \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon^2 & \epsilon \\ \epsilon & \epsilon^2 \end{pmatrix}$	(x, y)	$(x^2 - y^2, xy)$
A''	1	1	1	-1	-1	-1	z	
E''	$\begin{pmatrix} 1 & \epsilon & \epsilon^2 \\ 1 & \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon & \epsilon^2 \\ \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon^2 & \epsilon \\ \epsilon & \epsilon^2 \end{pmatrix}$	-1	$\begin{pmatrix} \epsilon & \epsilon^2 \\ \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon^2 & \epsilon \\ \epsilon & \epsilon^2 \end{pmatrix}$	(R_x, R_y)	(xz, yz)

C_{4h} ($4/m$)	E	C_4	C_2	C_4^3	i	S_4^2	σ_h	S_4		
A_g	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
B_g	1	-1	1	-1	1	-1	1	-1		$x^2 - y^2, xy$
E_g	$\begin{pmatrix} 1 & i & -1 & -i \\ 1 & -i & -1 & i \end{pmatrix}$	$\begin{pmatrix} i & -i \\ -i & i \end{pmatrix}$	$\begin{pmatrix} -1 & -1 \\ -1 & -1 \end{pmatrix}$	$\begin{pmatrix} -i & i \\ i & -i \end{pmatrix}$	1	$\begin{pmatrix} i & -i \\ -i & i \end{pmatrix}$	$\begin{pmatrix} -1 & -1 \\ -1 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & -1 \\ -1 & -1 \end{pmatrix}$	(R_x, R_y)	(xz, yz)
A_u	1	1	1	1	-1	-1	-1	-1	z	
B_u	1	-1	1	-1	-1	1	-1	1		
E_u	$\begin{pmatrix} 1 & i & -1 & -i \\ 1 & -i & -1 & i \end{pmatrix}$	$\begin{pmatrix} i & -i \\ -i & i \end{pmatrix}$	$\begin{pmatrix} -1 & -1 \\ -1 & -1 \end{pmatrix}$	$\begin{pmatrix} -i & i \\ i & -i \end{pmatrix}$	-1	$\begin{pmatrix} i & -i \\ -i & i \end{pmatrix}$	$\begin{pmatrix} -1 & -1 \\ -1 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & -1 \\ -1 & -1 \end{pmatrix}$	(x, y)	

 $D_n (n = 2, 3, 4)$

D_2 (222)	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A	1	1	1	1		x^2, y^2, z^2
B_1	1	1	-1	-1	z, R_z	xy
B_2	1	-1	1	-1	y, R_y	xz
B_3	1	-1	-1	1	x, R_x	yz

D_3 (32)	E	$2C_3$	$3C_2$		
A_1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	-1	z, R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

D_4 (422)	E	$2C_4$	$C_2(=C_4^2)$	$2C_2'$	$2C_2''$	
A_1	1	1	1	1	1	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	z, R_z
B_1	1	-1	1	1	-1	$x^2 - y^2$
B_2	1	-1	1	-1	1	xy
E	2	0	-2	0	0	$(x, y)(R_x, R_y)$ (xz, yz)

Cubic Groups

T_d ($\bar{4}3m$)	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2,$ $x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

O_h ($m\bar{3}m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($=C_4^2$)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	$(2z^2 - x^2 - y^2,$ $x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ	$\eta^\pm = \frac{1}{2}(1 \pm 5^{1/2})$
A_g	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
T_{1g}	3	η^+	η^-	0	-1	3	η^-	η^+	0	-1	(R_x, R_y, R_z)
T_{2g}	3	η^-	η^+	0	-1	3	η^+	η^-	0	-1	
G_g	4	-1	-1	1	0	4	-1	-1	1	0	
H_g	5	0	0	-1	1	5	0	0	-1	1	$(2z^2 - x^2 - y^2,$ $x^2 - y^2,$ $xy, yz, zx)$
A_u	1	1	1	1	1	-1	-1	-1	-1	-1	
T_{1u}	3	η^+	η^-	0	-1	-3	$-\eta^-$	$-\eta^+$	0	1	(x, y, z)
T_{2u}	3	η^-	η^+	0	-1	-3	$-\eta^+$	$-\eta^-$	0	1	
G_u	4	-1	-1	1	0	-4	1	1	-1	0	
H_u	5	0	0	-1	1	-5	0	0	1	-1	

3 Nuclear Vibrations

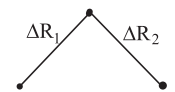
3.1 Normal vibrations

The motions or distributions of nuclei (atoms) in molecules with N atoms is described classically or quantum mechanically with the help of the respective 3N cartesian coordinates. One can construct 3N linear independent linear combinations of the original coordinates, which correspond to the 3 overall translations of the whole molecule in x, y, z -direction; to 3 overall rotations of the molecule around the 3 "main axes", which are equivalent to the set of rotations around the 3 cartesian axes, R_x, R_y, R_z . In the case of a linear molecule, the rotation around the molecular axis is not a nuclear rotation, but a rotation of the electric shell (rotation of a nucleus around its own axis would mean another radioactive (γ) nuclear state of extremely high energy). So there are 3N-6 or -5 nuclear motions: vibrations, and possibly internal rotations, librations or other large amplitude motions. Concerning comparably rigid molecules at comparably low energies, the 3N-6 or -5 internal motions are symmetry-adapted, uncoupled, so-called "normal vibrations". They are determined through the coupling of individual bond variations. Here are two simple examples:

3.2 Quadratic forms

1) H₂O bond stretches:

The potential energy varies approximately as $E = k/2 \cdot (\Delta R_1^2 + \Delta R_2^2) + \kappa \cdot \Delta R_1 \cdot \Delta R_2$ in terms of (mass-weighted) internal coordinates ΔR_i . This quadratic form can be written as

$$E = 1/2 \cdot \langle \Delta R_1, \Delta R_2 | \begin{bmatrix} k & \kappa \\ \kappa & k \end{bmatrix} | \begin{matrix} \Delta R_1 \\ \Delta R_2 \end{matrix} \rangle = 1/2 \cdot \langle \nu_1, \nu_2 | \begin{bmatrix} k + \kappa & 0 \\ 0 & k - \kappa \end{bmatrix} | \begin{matrix} \nu_1 \\ \nu_2 \end{matrix} \rangle$$


$k \pm \kappa$ are the eigenvalues of the force constants matrix, and ν_i are the eigenvectors, the "normal" coordinates $\nu_1 = (\Delta R_1 + \Delta R_2)/\sqrt{2}$, $\nu_2 = (\Delta R_1 - \Delta R_2)/\sqrt{2}$



2) H₂O breathing and bending:

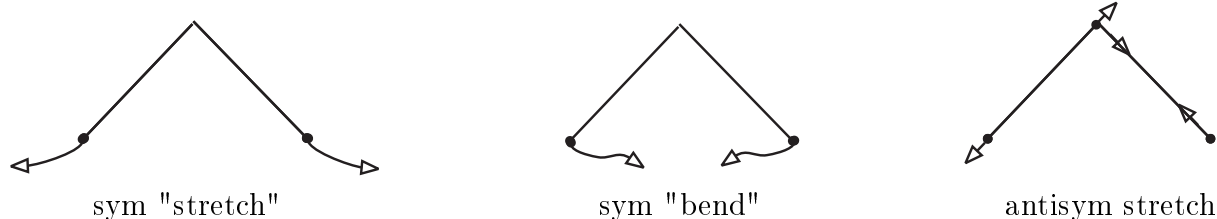
$$E = 1/2 \cdot k_{br} \cdot (\nu_1)^2 + 1/2 \cdot k_{bd} \cdot (\Delta\alpha)^2 + \gamma \cdot \nu_1 \cdot \Delta\alpha$$

$$E = 1/2 \cdot \langle \nu_1, \Delta\alpha | \begin{bmatrix} k_{br} & \gamma \\ \gamma & k_{bd} \end{bmatrix} | \begin{matrix} \nu_1 \\ \Delta\alpha \end{matrix} \rangle = 1/2 \cdot \langle \nu_+, \nu_- | \begin{bmatrix} k_+ & 0 \\ 0 & k_- \end{bmatrix} | \begin{matrix} \nu_+ \\ \nu_- \end{matrix} \rangle$$

$$\kappa_{+,-} = (k_{br} + k_{bd})/2 \pm \sqrt{(k_{br} - k_{bd})^2/4 + \gamma^2} \approx k_{br} + \gamma^2/(k_{br} + k_{bd}) \text{ or } k_{bd} - \gamma^2/(k_{br} - k_{bd}) .$$

Note: In lowest order of approximation, the motion of N atoms is described by about $4.5(N - 2)^2$ general force constants. This can be reduced to $3(N - 2)$ normal force constants.

Note: The basic independent motion types of a molecule are symmetry adapted mixtures of all possible internal motions. Example: H₂O



3.3 Symmetry Analysis

The character of symmetry operations S is independent of the directions of the motional coordinates of each atom. Therefore choose the cartesian coordinates of every atom in each case of S in the most appropriate manner.

$$\chi(S) = N_{fix} \cdot (2 \cdot \cos \phi \pm 1)$$

N_{fix} = number of nuclei not moved from their position by S ; ϕ = angle of rotation (C_1 : 0° ; C_2 : 180° ; etc; σ : 0° ; i : 180°); +1 for pure rotation, -1 for "improper" mirror rotation ($\sigma = S_1$, $i = S_2$, etc.).

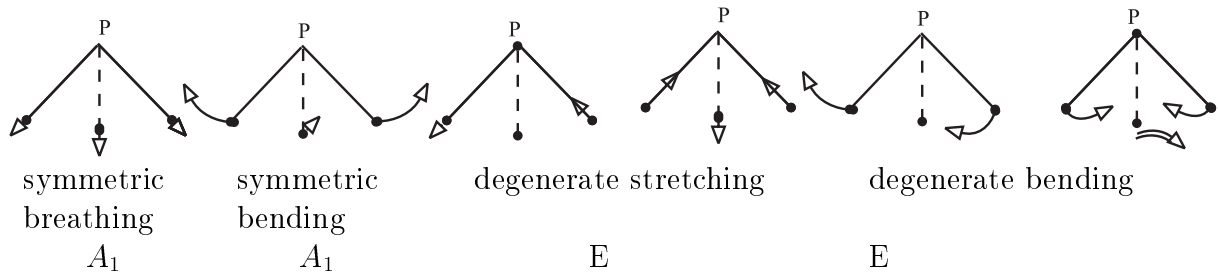
Example: PH₃

C_{3v}	E	$2C_3$	$3\sigma_v$	g=6
A_1	1	1	1	$z; x^2 + y^2; z^2$
A_2	1	1	-1	R_z
E	2	-1	0	$(x, y); (R_x, R_y); (xy, x^2 - y^2)(xz, yz)$
N_{fix}	4	1	2	
n_k	1	2	3	
ϕ	0	120°	0	
$2 \cos \phi$	2	-1	2	
± 1	+1	+1	-1	
$2 \cos \phi \pm 1$	3	0	1	
$N_{fix} \cdot n_k(2c \pm 1)$	12	0	6	
$\langle A_1 \chi \rangle$	12		+6	18:6=3
$\langle A_2 \chi \rangle$	12		-6	6:6=1
$\langle E \chi \rangle$	24		+0	24:6=4

$$4 \text{ atoms} = 12 \text{ motions} = 3A_1 + A_2 + 4E$$

Translations are $x, y, z = A_1 + E$; Rotations are $R_x, R_y, R_z = A_2 + E$

Remaining vibrations: $2A_1 + 2E$ - There are $3N-6=6$ vibrational freedoms, giving rise to 4 normal modes, two nondegenerate symmetric ones and two degenerate skew ones.



IR active vibrations (in lowest order of approximation, at low temperatures) are those of x, y, z -type: A_1, E . Raman active are those of x^2, xy etc. type: A_1, E (in this case accidentally the same as IR). In the present special example, all vibrations are detectable in both kinds of spectra.

The emission and absorption probabilities (intensities) of electromagnetic spectra [rotational excitation in the microwave (MW) region; vibrational excitation in the infrared region (IR); valence electronic absorption or fluorescence or vibrational inelastic photon scattering (Raman) in the visible and near ultraviolet region (VIS-UV); core electronic excitation in the far UV and X-ray region (X-UV)] are proportional to the value squared of the transition moment (transition matrix element):

$$\sim |\langle \psi_i | \widehat{O}_p | \psi_f \rangle|^2$$

ψ_i and ψ_f are the wave functions of the initial and final nuclear (vibrational, rotational) and electronic states of the transition. And \widehat{O}_p is the operator of interaction of the electric wave with the electronic and nuclear charges, the largest contribution usually being $\sim \sqrt{I} \cdot \vec{r} \cdot (-e \text{ or } +Ze)$ for absorption or emission, and the respective product for the absorption-emission-Raman-effect.

Symmetry

SS 2002: PROFS. ENGELEN AND SCHWARZ

Mittwochs, 8:22-10 h, AR-G113

Fragen-Termin Montags, 12:15h, AR-K616

Übungs-Abgabe Montag abends, gelber Holzbriefkasten AR-K602

Part I: Finite Systems (§§1-4, SCHWARZ)

Part II: Periodic Systems (§§5-8, ENGELEN)

0 Introduction (ENGELEN, 17.4.)

1 Symmetry Groups (SCHWARZ, 24.4.)

1.1 Groups and Classes

1.2 Symmetry Transformations

1.3 Point Groups, Chirality (SCHWARZ, 2.5., Ü)

2 Matrix Representations (SCHWARZ, 8.5.)

2.1 Operations and Matrices

2.2 Reduction to Irreducible Representations

2.3 Group Tables and Characters (SCHWARZ, 17.5.)

3 Symmetry of Nuclear Vibrations (SCHWARZ, 22.5.)

3.1 Normal Vibrations

3.2 Quadratic Forms

3.2 Harmonic Normal Vibrations

3.3 Infrared and Raman Transitions (SCHWARZ, 29.5.)

4 Symmetry of Electronic Orbitals

4.1 Basics

4.2 The Non-Crossing Rule (SCHWARZ, 12.6.)

4.3 The Woodward-Hoffmann-Rules

4.4 Molecular Symmetry Orbitals

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: $[x \cdot, d/dx] = x \cdot d/dx - d/dx \cdot x \cdot = \underline{1}$. !!

{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 group 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 definition 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 $T_{x \rightarrow x'}$, 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:

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

Example: For the rotation of the plane

$$x = x' \cdot \cos \phi + y' \cdot \sin \phi; y = y' \cdot \cos \phi - x' \cdot \sin \phi, \text{ i.e. } \vec{x} = C^\phi \cdot \vec{x}'$$

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:

$$n\text{-fold rotations } C_n : (C_n)^n = E, (C_n)^{n-1} = C_n^{-1}$$

$$\text{mirror reflection (Spiegelung) } \sigma : \sigma^2 = E, \sigma^{-1} = \sigma$$

$$\text{rotational reflection (Drehspiegelung) } S_n = C_n \cdot \sigma_h = \sigma_h \cdot C_n:$$

$$S_1 = \sigma = I_2; S_2 = i = I_1 \text{ (inversion); } S_3 = I_6^{-1}; S_3^6 = E; S_4 = I_4^{-1}$$

$$I_n \text{ (rotational inversion, Drehinversion) } = C_n \cdot i = i \cdot C_n$$

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 (Et-FCl)
only a mirror plane	C_s (NOCl)
only an inversion center	C_i ((CHBrCl) ₂)
only a symmetry axis	C_n ($n = 2, 3, \dots$) (rigid H ₂ O ₂)
vertical C_n and horizontal σ , also S_n	C_{nh} (CHCl) ₂
vertical C_n and vertical σ 's (if n even, σ_v and σ_d):	C_{nv} (H ₂ O, PH ₃)
S_{2n} but no C_{2n} (but C_n)	S_{2n} (C ₈ H ₄ Cl ₄)
C_n and C_2 at 90°	D_n (MO _x 3)
C_n and $C_2 \perp$ and σ_h (and S_n and σ_v)	D_{nh} (C ₆ H ₆)
C_n and $C_2 \perp$ and vertical σ_d and S_n but no σ_h	D_{nd} (H ₂ C ₃ H ₂)
"linear" (cylindrical)	$C_{\infty v}, D_{\infty h}$ (HCl, N ₂)
Platonic bodies (equilateral surfaces)	
3 triangles at each corner	Tetrahedron – T, T_h, T_d (CH ₄)
4 triangles at each corner	Octahedron – O, O_h (ML ₆)
5 triangles at each corner	Ikosaeder – I, I_h (B ₁₂ H ₁₂)
3 squares at each corner	Hexaeder or cube – O_h (!) (C ₈ H ₈)
3 pentagons at each corner	Dodekaeder – I_h (!) N ₂₀
sphere	– O_3 (Ar)

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 possess any S_n or I_n . Systems with symmetry group C_n or D_n may be chiral. Asymmetric carbon atoms or asymmetric atoms are neither necessary nor sufficient 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, are 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.

2 Matrix Representations

2.1 Vectors, Operations, Matrices

See section 10 of Physikalische and Theoretische Chemie I. Nuclear positions and motions are described in the classical approximation by 3-dimensional Euklidian vectors $\vec{f}(t)$; and nuclei and electrons at the quantum level by wave functions (= state vectors $\vec{f}(x, t)$ in ∞ -dimensional Hilbert space). The natural laws for stationary states \vec{g} can be formulated most generally as $\mathcal{H}(x) \circ \vec{g}_n(x) = 0$, where \vec{g}_{nm} ($m = 1$ to d_n), the respective energy or frequency λ_n are the eigen-solutions.

If \mathcal{S} is a symmetry operation of the description formula of the system, $\mathcal{S}^{-1} = \mathcal{H}\mathcal{S} = \mathcal{H}$, i.e., \mathcal{H} is invariant under \mathcal{S} , then it follows, from $\mathcal{H}\vec{g} = 0$ that $\mathcal{H}\mathcal{S}\mathcal{S}^{-1}\vec{g} = 0 \rightarrow (\mathcal{S}^{-1}\mathcal{H}\mathcal{S})(\mathcal{S}^{-1}\vec{g}) = 0 \rightarrow \mathcal{H}(\mathcal{S}\vec{g}) = 0$

A symmetry transformed state vector is an equivalent vector, any $\mathcal{S}\vec{g}_{nm}$ is also an eigen-solution with the same λ_n as \vec{g}_{nm} .

Example: The atomic nuclear Coulomb potential is rotationally symmetric. Therefore the states of atoms are transformed by rotations into states of the same energy. A rotated p-orbital is also one of the p-state-manifold.

If \vec{g}_n is nondegenerate and real, the state vector is either symmetric: $\mathcal{S}\vec{g}_n = \vec{g}_n \cdot +1$, or it is antisymmetric: $\mathcal{S}\vec{g}_n = \vec{g}_n \cdot -1$. In the case of degenerate state vectors \vec{g}_{nm} $\mathcal{S}\vec{g}_{nm} = \sum_i \vec{g}_{ni} \cdot D_{im}$. D_{im} is a matrix representation matrix of \mathcal{S} . In the nondegenerate case, D is a 1×1 -matrix.

If \vec{g}_{nm} is an orthonormal set of d_n degenerate eigenvectors, then any complete orthonormal linear combination set of them is an equivalent set. The values of the representation matrix elements D_{nm} are changed, but the trace (Spur) $\sum_i D_{ii} = \chi_n$ is unchanged. χ_n is characteristic for the set of eigenvectors \vec{g}_{nm} corresponding to λ_n .

The symmetry of the eigensolutions to λ_n is uniquely specified by the $\chi_n(\mathcal{S})$, where the \mathcal{S} are the g different symmetry operations of the symmetry group. $\vec{\chi}$ is the g -dimensional character vector. The symmetry species (Rasse is named by a (lower or upper case) letter, see the table.

2.2 Irreducible Representations

There are just as many different symmetry types (or irreducible representations) Γ as there are different classes of the group, no more. There is always the unit class (E), and the totally symmetric, one-dimensional species $\vec{\chi} = (1, 1, \dots, 1)$. The dimensions of species

Γ are $\chi^\Gamma(E)$, these are the possible degeneracies of energies and frequencies of the system. The symmetry group determines the degeneracy pattern of stationary states. Since equivalent \mathcal{S} have the same character, only the "contracted" character vectors are given in the group tables. The character vectors $\vec{\chi}$ of different species a, b are orthonormal:

$$\langle \chi^a | \chi^b \rangle = \sum_s \chi^a(\mathcal{S})^* \cdot \chi^b(\mathcal{S}) = \sum_k \chi^a(\mathcal{K})^* \cdot \chi^b(\mathcal{K}) \cdot n_k = g \cdot \delta_{ab} \quad (2.1)$$

where n_k is the number of equivalent symmetry operations in equivalence class \mathcal{K} , and $\delta_{ab} = 1$ for $a = b$ and 0 for $a \neq b$. Given several states with their $d_1 + d_2 + \dots = d$ state function, or given a set of basis functions describing several states $1, 2, \dots$, the the representation matrices are $d \times d$ -dimensional, and the character vector is $\vec{\chi} = \vec{\chi}^1 + \vec{\chi}^2 + \dots$. "The reducible matrix representation consists of several irreducible components". Sometimes the same species γ occurs several (n_γ) times:

$$\vec{\chi} = \sum_\gamma \vec{\chi}^\gamma \cdot n_\gamma \quad (2.2)$$

From equations 2.1 and 2.2 follows

$$n_\gamma = \langle \chi^\gamma | \chi \rangle / g = 1/g \cdot \sum_k \chi^\gamma(\mathcal{K}) \cdot \chi(\mathcal{K}) \cdot n_k \quad (2.3)$$

With this important formula we can determine, which types and numbers of eigenstates exist in electronic (orbitals, state function) and nuclear systems (normal vibrations).

Example: Given a system with C_{3v} symmetry (e.g. PH_3), the group consists of (E), $(C_3, C_3^2) = 2C_3$, $(\sigma'_v, \sigma''_v, \sigma'''_v) = 3\sigma_v$. As basis we choose the z-shifts of the 4 nuclei, or 4-atomic s-valence orbitals. The 4×4 -matrix representation of the symmetry group operators is:

$$D : \begin{array}{c} \begin{array}{c|c|c|c} E & C_3 & C_3^2 & \sigma'_v \\ \hline \begin{array}{cccc} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{array} & \begin{array}{cccc} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{array} & \begin{array}{cccc} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{array} & \begin{array}{cccc} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{array} & \begin{array}{cccc} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{array} & \begin{array}{cccc} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{array} \end{array} \end{array}$$

$$\chi : \quad 4 \quad 1 \quad 1 \quad 2 \quad 2 \quad 2$$

Short version of the character vector: $\vec{\chi} = (4, 1, 2)$. We transform to the "symmetry

adapted" basis with the help of the transformation matrix $T = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{3} & 0 & 2/\sqrt{6} \\ 0 & 1/\sqrt{3} & 1/\sqrt{2} & -1/\sqrt{6} \\ 0 & 1/\sqrt{3} & -1/\sqrt{2} & -1/\sqrt{6} \end{pmatrix}$.

The transformed matrix representation is

$$D^T : \begin{array}{c} \begin{array}{c|c|c} \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array} & \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1/2 + \sqrt{3}/2 \end{array} & \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -\sqrt{3}/2 - 1/2 \end{array} \\ \hline \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1/2 - \sqrt{3}/2 \end{array} & \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \sqrt{3}/2 - 1/2 \end{array} & \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array} \\ \hline \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1/2 + \sqrt{3}/2 \end{array} & \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1/2 - \sqrt{3}/2 \end{array} & \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -\sqrt{3}/2 + 1/2 \end{array} \end{array} \end{array}$$

$$\chi : \quad 4=1+1+2 \quad 1=1+1-1 \quad 1=1+1-1 \quad 2=1+1+0 \quad 2=1+1+0 \quad 2=1+1+0$$

With the above given transformation trick, we have "reduced" the 4-dimensional reducible representation into its irreducible components: $\chi = A_1 + A_1 + E = 2A_1 + E$

Applying eq. (2.3) we obtain (Note: the n_γ must be 0,1,2,...):

C_{3v}	$1 \cdot E$	$2 \cdot C_3$	$3 \cdot \sigma_v$	$g=6$
A_1	1	1	1	
A_2	1	1	-1	
E	2	-1	0	
χ	4	1	2	$2A_1 + E$

A_1	$1 \cdot 4$	$+1 \cdot 2 \cdot 1$	$+1 \cdot 3 \cdot 2$	$12/6=2$
A_2	$1 \cdot 4$	$+1 \cdot 2 \cdot 1$	$-1 \cdot 3 \cdot 2$	0
E	$2 \cdot 4$	$-1 \cdot 2 \cdot 1$	$+0 \cdot 3 \cdot 2$	$6/6=1$

2.3 Group Character Tables

Point Symmetry Group:
 Schoenflies-symbol
 Hermann-Mauguin-symbol

Equivalence Classes of symmetry operations

Irreducible Representations = Species = Rasse
 A, Σ, S - one-dimensional, +1 for C_n
 B - one-dimensional, -1 for C_n
 $E, \Pi, \Delta, \Phi, \dots$ - two-dimensional
 T, P - three-dimensional
 G - four-dimensional
 H, D - five-dimensional
 g, u - gerade/ungerade for i (!!)
 1, 2 - +1 or -1 for σ_v (not unique, if σ_v and σ_d)

Character = sum of values (trace) concerning a symmetry transformation (of a given class) of degenerate eigenvectors into itself.

Examples for the species: translation or dipole operators; rotation operators; quadruple operators.

$D_{nd} (n = 2, 3)$

$D_{2d} = V_d$ ($\bar{4}2m$)	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	$x^2 - y^2$
B_1	1	-1	1	1	-1	z	xy
B_2	1	-1	1	-1	1	(x, y)	(xz, yz)
E	2	0	-2	0	0	(R_x, R_y)	

D_{3d} ($\bar{3}m$)	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	-1	1	1	-1	R_z	$x^2 - y^2, xy$
E_g	2	-1	0	2	-1	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	-1	-1	-1		
A_{2u}	1	1	-1	-1	-1	1	z	
E_u	2	-1	0	-2	1	0	(x, y)	

C_{nv} ($n = 2, 3, 4, 5, 6, \infty$)

C_{2v} ($2mm$)	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

C_{3v} ($3m$)	E	$2C_3$	$3\sigma_v$			
A_1	1	1	1	z		$x^2 + y^2, z^2$
A_2	1	1	-1	R_z		
E	2	-1	0	$(x, y)(R_x, R_y)$		$(x^2 - y^2, xy)(xz, yz)$

C_{4v} ($4mm$)	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$		
A_1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	R_z	
E_1	2	$2 \cos 72^\circ$	$2 \cos 144^\circ$	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	$2 \cos 144^\circ$	$2 \cos 72^\circ$	0		$(x^2 - y^2, xy)$

C_{6v} ($6mm$)	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$		
A_1	1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	-1		
B_2	1	-1	1	-1	-1	1		
E_1	2	1	-1	-2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$

$C_{\infty v}$	E	$2C_\infty^\phi$	\dots	$\infty\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	\dots	1	z	$x^2 + y^2, z^2$
$A_2 \equiv \Sigma^-$	1	1	\dots	-1	R_z	
$E_1 \equiv \Pi$	2	$2 \cos \phi$	\dots	0	$(x, y)(R_x, R_y)$	(xz, yz)
$E_2 \equiv \Delta$	2	$2 \cos 2\phi$	\dots	0		$(x^2 - y^2, xy)$
$E_3 \equiv \Phi$	2	$2 \cos 3\phi$	\dots	0		
\dots	\dots	\dots	\dots	\dots		

$C_{nh} (n = 2, 3, 4)$

C_{2h} (2/m)	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

C_{3h} (6)	E	C_3	C_3^2	σ_h	S_3	S_3^5		$\epsilon = \exp(2\pi i/3)$
A'	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
E'	$\begin{pmatrix} 1 & \epsilon & \epsilon^2 \\ 1 & \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon & \epsilon^2 \\ \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon^2 & \epsilon \\ \epsilon & \epsilon^2 \end{pmatrix}$	1	ϵ	ϵ^2	(x, y)	$(x^2 - y^2, xy)$
A''	1	1	1	-1	-1	-1	z	
E''	$\begin{pmatrix} 1 & \epsilon & \epsilon^2 \\ 1 & \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon & \epsilon^2 \\ \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon^2 & \epsilon \\ \epsilon & \epsilon^2 \end{pmatrix}$	-1	$-\epsilon$	$-\epsilon^2$	(R_x, R_y)	(xz, yz)

C_{4h} (4/m)	E	C_4	C_2	C_4^3	i	S_4^2	σ_h	S_4		
A_g	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
B_g	1	-1	1	-1	1	-1	1	-1		$x^2 - y^2, xy$
E_g	$\begin{pmatrix} 1 & i & -1 & -i \\ 1 & -i & -1 & i \end{pmatrix}$	$\begin{pmatrix} i & -i \\ -i & i \end{pmatrix}$	$\begin{pmatrix} -1 & -i \\ -1 & i \end{pmatrix}$	$\begin{pmatrix} -i & -1 \\ i & -1 \end{pmatrix}$	1	i	$-i$	-1	(R_x, R_y)	(xz, yz)
A_u	1	1	1	1	-1	-1	-1	-1	z	
B_u	1	-1	1	-1	-1	1	-1	1		
E_u	$\begin{pmatrix} 1 & i & -1 & -i \\ 1 & -i & -1 & i \end{pmatrix}$	$\begin{pmatrix} i & -i \\ -i & i \end{pmatrix}$	$\begin{pmatrix} -1 & -i \\ -1 & i \end{pmatrix}$	$\begin{pmatrix} -i & -1 \\ i & -1 \end{pmatrix}$	-1	i	$-i$	-1	(x, y)	

 $D_n (n = 2, 3, 4)$

D_2 (222)	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A	1	1	1	1		x^2, y^2, z^2
B_1	1	1	-1	-1	z, R_z	xy
B_2	1	-1	1	-1	y, R_y	xz
B_3	1	-1	-1	1	x, R_x	yz

D_3 (32)	E	$2C_3$	$3C_2$		
A_1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	-1	z, R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

D_4 (422)	E	$2C_4$	$C_2(=C_4^2)$	$2C_2'$	$2C_2''$	
A_1	1	1	1	1	1	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	z, R_z
B_1	1	-1	1	1	-1	$x^2 - y^2$
B_2	1	-1	1	-1	1	xy
E	2	0	-2	0	0	$(x, y)(R_x, R_y)$ (xz, yz)

Cubic Groups

T_d ($\bar{4}3m$)	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2,$ $x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

O_h ($m\bar{3}m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($=C_4^2$)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	$(2z^2 - x^2 - y^2,$ $x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ	$\eta^\pm = \frac{1}{2}(1 \pm 5^{1/2})$
A_g	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
T_{1g}	3	η^+	η^-	0	-1	3	η^-	η^+	0	-1	(R_x, R_y, R_z)
T_{2g}	3	η^-	η^+	0	-1	3	η^+	η^-	0	-1	
G_g	4	-1	-1	1	0	4	-1	-1	1	0	
H_g	5	0	0	-1	1	5	0	0	-1	1	$(2z^2 - x^2 - y^2,$ $x^2 - y^2,$ $xy, yz, zx)$
A_u	1	1	1	1	1	-1	-1	-1	-1	-1	
T_{1u}	3	η^+	η^-	0	-1	-3	$-\eta^-$	$-\eta^+$	0	1	(x, y, z)
T_{2u}	3	η^-	η^+	0	-1	-3	$-\eta^+$	$-\eta^-$	0	1	
G_u	4	-1	-1	1	0	-4	1	1	-1	0	
H_u	5	0	0	-1	1	-5	0	0	1	-1	

3 Nuclear Vibrations

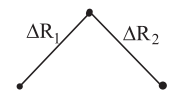
3.1 Normal vibrations

The motions or distributions of nuclei (atoms) in molecules with N atoms is described classically or quantum mechanically with the help of the respective 3N cartesian coordinates. One can construct 3N linear independent linear combinations of the original coordinates, which correspond to the 3 overall translations of the whole molecule in x, y, z -direction; to 3 overall rotations of the molecule around the 3 "main axes", which are equivalent to the set of rotations around the 3 cartesian axes, R_x, R_y, R_z . In the case of a linear molecule, the rotation around the molecular axis is not a nuclear rotation, but a rotation of the electric shell (rotation of a nucleus around its own axis would mean another radioactive (γ) nuclear state of extremely high energy). So there are 3N-6 or -5 nuclear motions: vibrations, and possibly internal rotations, librations or other large amplitude motions. Concerning comparably rigid molecules at comparably low energies, the 3N-6 or -5 internal motions are symmetry-adapted, uncoupled, so-called "normal vibrations". They are determined through the coupling of individual bond variations. Here are two simple examples:

3.2 Quadratic forms

1) H₂O bond stretches:

The potential energy varies approximately as $E = k/2 \cdot (\Delta R_1^2 + \Delta R_2^2) + \kappa \cdot \Delta R_1 \cdot \Delta R_2$ in terms of (mass-weighted) internal coordinates ΔR_i . This quadratic form can be written as

$$E = 1/2 \cdot \langle \Delta R_1, \Delta R_2 | \begin{bmatrix} k & \kappa \\ \kappa & k \end{bmatrix} | \begin{matrix} \Delta R_1 \\ \Delta R_2 \end{matrix} \rangle = 1/2 \cdot \langle \nu_1, \nu_2 | \begin{bmatrix} k + \kappa & 0 \\ 0 & k - \kappa \end{bmatrix} | \begin{matrix} \nu_1 \\ \nu_2 \end{matrix} \rangle$$


$k \pm \kappa$ are the eigenvalues of the force constants matrix, and ν_i are the eigenvectors, the "normal" coordinates $\nu_1 = (\Delta R_1 + \Delta R_2)/\sqrt{2}$, $\nu_2 = (\Delta R_1 - \Delta R_2)/\sqrt{2}$



2) H₂O breathing and bending:

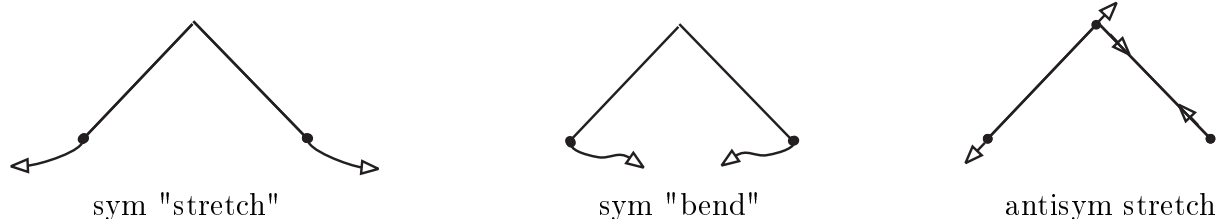
$$E = 1/2 \cdot k_{br} \cdot (\nu_1)^2 + 1/2 \cdot k_{bd} \cdot (\Delta\alpha)^2 + \gamma \cdot \nu_1 \cdot \Delta\alpha$$

$$E = 1/2 \cdot \langle \nu_1, \Delta\alpha | \begin{bmatrix} k_{br} & \gamma \\ \gamma & k_{bd} \end{bmatrix} | \begin{matrix} \nu_1 \\ \Delta\alpha \end{matrix} \rangle = 1/2 \cdot \langle \nu_+, \nu_- | \begin{bmatrix} k_+ & 0 \\ 0 & k_- \end{bmatrix} | \begin{matrix} \nu_+ \\ \nu_- \end{matrix} \rangle$$

$$\kappa_{+,-} = (k_{br} + k_{bd})/2 \pm \sqrt{(k_{br} - k_{bd})^2/4 + \gamma^2} \approx k_{br} + \gamma^2/(k_{br} + k_{bd}) \quad \text{or} \quad k_{bd} - \gamma^2/(k_{br} - k_{bd}) .$$

Note: In lowest order of approximation, the motion of N atoms is described by about $4.5(N - 2)^2$ general force constants. This can be reduced to $3(N - 2)$ normal force constants.

Note: The basic independent motion types of a molecule are symmetry adapted mixtures of all possible internal motions. Example: H₂O



3.3 Symmetry Analysis

The character of symmetry operations S is independent of the directions of the motional coordinates of each atom. Therefore choose the cartesian coordinates of every atom in each case of S in the most appropriate manner.

$$\chi(S) = N_{fix} \cdot (2 \cdot \cos \phi \pm 1)$$

N_{fix} = number of nuclei not moved from their position by S ; ϕ = angle of rotation (C_1 : 0° ; C_2 : 180° ; etc; σ : 0° ; i : 180°); +1 for pure rotation, -1 for "improper" mirror rotation ($\sigma = S_1$, $i = S_2$, etc.).

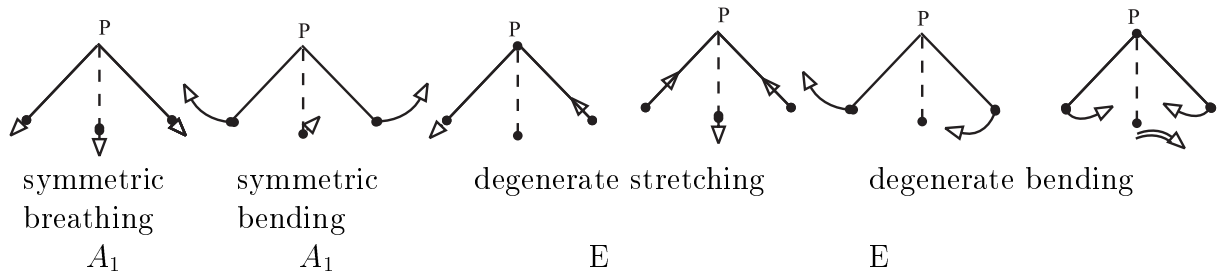
Example: PH₃

C_{3v}	E	$2C_3$	$3\sigma_v$	g=6
A_1	1	1	1	$z; x^2 + y^2; z^2$
A_2	1	1	-1	R_z
E	2	-1	0	$(x, y); (R_x, R_y); (xy, x^2 - y^2)(xz, yz)$
N_{fix}	4	1	2	
n_k	1	2	3	
ϕ	0	120°	0	
$2 \cos \phi$	2	-1	2	
± 1	+1	+1	-1	
$2 \cos \phi \pm 1$	3	0	1	
$N_{fix} \cdot n_k(2c \pm 1)$	12	0	6	
$\langle A_1 \chi \rangle$	12		+6	18:6=3
$\langle A_2 \chi \rangle$	12		-6	6:6=1
$\langle E \chi \rangle$	24		+0	24:6=4

$$4 \text{ atoms} = 12 \text{ motions} = 3A_1 + A_2 + 4E$$

Translations are $x, y, z = A_1 + E$; Rotations are $R_x, R_y, R_z = A_2 + E$

Remaining vibrations: $2A_1 + 2E$ - There are $3N-6=6$ vibrational freedoms, giving rise to 4 normal modes, two nondegenerate symmetric ones and two degenerate skew ones.



IR active vibrations (in lowest order of approximation, at low temperatures) are those of x, y, z -type: A_1, E . Raman active are those of x^2, xy etc. type: A_1, E (in this case accidentally the same as IR). In the present special example, all vibrations are detectable in both kinds of spectra.

The emission and absorption probabilities (intensities) of electromagnetic spectra [rotational excitation in the microwave (MW) region; vibrational excitation in the infrared region (IR); valence electronic absorption or fluorescence or vibrational inelastic photon scattering (Raman) in the visible and near ultraviolet region (VIS-UV); core electronic excitation in the far UV and X-ray region (X-UV)] are proportional to the value squared of the transition moment (transition matrix element):

$$\sim |\langle \psi_i | \widehat{O}_p | \psi_f \rangle|^2$$

ψ_i and ψ_f are the wave functions of the initial and final nuclear (vibrational, rotational) and electronic states of the transition. And \widehat{O}_p is the operator of interaction of the electric wave with the electronic and nuclear charges, the largest contribution usually being $\sim \sqrt{I} \cdot \vec{r} \cdot (-e \text{ or } +Ze)$ for absorption or emission, and the respective product for the absorption-emission-Raman-effect.

Symmetry

SS 2002: PROFS. ENGELEN AND SCHWARZ

Mittwochs, 8:22-10 h, AR-G113

Fragen-Termin Montags, 12:15h, AR-K616

Übungs-Abgabe Montag abends, gelber Holzbriefkasten AR-K602

Part I: Finite Systems (§§1-4, SCHWARZ)

Part II: Periodic Systems (§§5-8, ENGELEN)

0 Introduction (ENGELEN, 17.4.)

1 Symmetry Groups (SCHWARZ, 24.4.)

1.1 Groups and Classes

1.2 Symmetry Transformations

1.3 Point Groups, Chirality (SCHWARZ, 2.5., Ü)

2 Matrix Representations (SCHWARZ, 8.5.)

2.1 Operations and Matrices

2.2 Reduction to Irreducible Representations

2.3 Group Tables and Characters (SCHWARZ, 17.5.)

3 Symmetry of Nuclear Vibrations (SCHWARZ, 22.5.)

3.1 Normal Vibrations

3.2 Quadratic Forms

3.2 Harmonic Normal Vibrations

3.3 Infrared and Raman Transitions (SCHWARZ, 29.5.)

4 Symmetry of Electronic Orbitals

4.1 Basics

4.2 The Non-Crossing Rule (SCHWARZ, 12.6.)

4.3 The Woodward-Hoffmann-Rules

4.4 Molecular Symmetry Orbitals

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: $[x \cdot, d/dx] = x \cdot d/dx - d/dx \cdot x \cdot = \underline{1}$. !!

{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 group 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 definition 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 $T_{x \rightarrow x'}$, 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:

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

Example: For the rotation of the plane

$$x = x' \cdot \cos \phi + y' \cdot \sin \phi; y = y' \cdot \cos \phi - x' \cdot \sin \phi, \text{ i.e. } \vec{x} = C^\phi \cdot \vec{x}'$$

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:

$$n\text{-fold rotations } C_n : (C_n)^n = E, (C_n)^{n-1} = C_n^{-1}$$

$$\text{mirror reflection (Spiegelung) } \sigma : \sigma^2 = E, \sigma^{-1} = \sigma$$

$$\text{rotational reflection (Drehspiegelung) } S_n = C_n \cdot \sigma_h = \sigma_h \cdot C_n:$$

$$S_1 = \sigma = I_2; S_2 = i = I_1 \text{ (inversion); } S_3 = I_6^{-1}; S_3^6 = E; S_4 = I_4^{-1}$$

$$I_n \text{ (rotational inversion, Drehinversion) } = C_n \cdot i = i \cdot C_n$$

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 (Et-FCl)
only a mirror plane	C_s (NOCl)
only an inversion center	C_i ((CHBrCl) ₂)
only a symmetry axis	C_n ($n = 2, 3, \dots$) (rigid H ₂ O ₂)
vertical C_n and horizontal σ , also S_n	C_{nh} (CHCl) ₂
vertical C_n and vertical σ 's (if n even, σ_v and σ_d):	C_{nv} (H ₂ O, PH ₃)
S_{2n} but no C_{2n} (but C_n)	S_{2n} (C ₈ H ₄ Cl ₄)
C_n and C_2 at 90°	D_n (MO _x 3)
C_n and $C_2 \perp$ and σ_h (and S_n and σ_v)	D_{nh} (C ₆ H ₆)
C_n and $C_2 \perp$ and vertical σ_d and S_n but no σ_h	D_{nd} (H ₂ C ₃ H ₂)
"linear" (cylindrical)	$C_{\infty v}, D_{\infty h}$ (HCl, N ₂)
Platonic bodies (equilateral surfaces)	
3 triangles at each corner	Tetrahedron – T, T_h, T_d (CH ₄)
4 triangles at each corner	Octahedron – O, O_h (ML ₆)
5 triangles at each corner	Ikosaeder – I, I_h (B ₁₂ H ₁₂)
3 squares at each corner	Hexaeder or cube – O_h (!) (C ₈ H ₈)
3 pentagons at each corner	Dodekaeder – I_h (!) N ₂₀
sphere	– O_3 (Ar)

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 possess any S_n or I_n . Systems with symmetry group C_n or D_n may be chiral. Asymmetric carbon atoms or asymmetric atoms are neither necessary nor sufficient 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, are 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.

2 Matrix Representations

2.1 Vectors, Operations, Matrices

See section 10 of Physikalische and Theoretische Chemie I. Nuclear positions and motions are described in the classical approximation by 3-dimensional Euklidian vectors $\vec{f}(t)$; and nuclei and electrons at the quantum level by wave functions (= state vectors $\vec{f}(x, t)$ in ∞ -dimensional Hilbert space). The natural laws for stationary states \vec{g} can be formulated most generally as $\mathcal{H}(x) \circ \vec{g}_n(x) = 0$, where \vec{g}_{nm} ($m = 1$ to d_n), the respective energy or frequency λ_n are the eigen-solutions.

If \mathcal{S} is a symmetry operation of the description formula of the system, $\mathcal{S}^{-1} = \mathcal{H}\mathcal{S} = \mathcal{H}$, i.e., \mathcal{H} is invariant under \mathcal{S} , then it follows, from $\mathcal{H}\vec{g} = 0$ that $\mathcal{H}\mathcal{S}\mathcal{S}^{-1}\vec{g} = 0 \rightarrow (\mathcal{S}^{-1}\mathcal{H}\mathcal{S})(\mathcal{S}^{-1}\vec{g}) = 0 \rightarrow \mathcal{H}(\mathcal{S}\vec{g}) = 0$

A symmetry transformed state vector is an equivalent vector, any $\mathcal{S}\vec{g}_{nm}$ is also an eigen-solution with the same λ_n as \vec{g}_{nm} .

Example: The atomic nuclear Coulomb potential is rotationally symmetric. Therefore the states of atoms are transformed by rotations into states of the same energy. A rotated p-orbital is also one of the p-state-manifold.

If \vec{g}_n is nondegenerate and real, the state vector is either symmetric: $\mathcal{S}\vec{g}_n = \vec{g}_n \cdot +1$, or it is antisymmetric: $\mathcal{S}\vec{g}_n = \vec{g}_n \cdot -1$. In the case of degenerate state vectors \vec{g}_{nm} $\mathcal{S}\vec{g}_{nm} = \sum_i \vec{g}_{ni} \cdot D_{im}$. D_{im} is a matrix representation matrix of \mathcal{S} . In the nondegenerate case, D is a 1×1 -matrix.

If \vec{g}_{nm} is an orthonormal set of d_n degenerate eigenvectors, then any complete orthonormal linear combination set of them is an equivalent set. The values of the representation matrix elements D_{nm} are changed, but the trace (Spur) $\sum_i D_{ii} = \chi_n$ is unchanged. χ_n is characteristic for the set of eigenvectors \vec{g}_{nm} corresponding to λ_n .

The symmetry of the eigensolutions to λ_n is uniquely specified by the $\chi_n(\mathcal{S})$, where the \mathcal{S} are the g different symmetry operations of the symmetry group. $\vec{\chi}$ is the g -dimensional character vector. The symmetry species (Rasse is named by a (lower or upper case) letter, see the table.

2.2 Irreducible Representations

There are just as many different symmetry types (or irreducible representations) Γ as there are different classes of the group, no more. There is always the unit class (E), and the totally symmetric, one-dimensional species $\vec{\chi} = (1, 1, \dots, 1)$. The dimensions of species

Γ are $\chi^\Gamma(E)$, these are the possible degeneracies of energies and frequencies of the system. The symmetry group determines the degeneracy pattern of stationary states. Since equivalent \mathcal{S} have the same character, only the "contracted" character vectors are given in the group tables. The character vectors $\vec{\chi}$ of different species a, b are orthonormal:

$$\langle \chi^a | \chi^b \rangle = \sum_s \chi^a(\mathcal{S})^* \cdot \chi^b(\mathcal{S}) = \sum_k \chi^a(\mathcal{K})^* \cdot \chi^b(\mathcal{K}) \cdot n_k = g \cdot \delta_{ab} \quad (2.1)$$

where n_k is the number of equivalent symmetry operations in equivalence class \mathcal{K} , and $\delta_{ab} = 1$ for $a = b$ and 0 for $a \neq b$. Given several states with their $d_1 + d_2 + \dots = d$ state function, or given a set of basis functions describing several states $1, 2, \dots$, the the representation matrices are $d \times d$ -dimensional, and the character vector is $\vec{\chi} = \vec{\chi}^1 + \vec{\chi}^2 + \dots$. "The reducible matrix representation consists of several irreducible components". Sometimes the same species γ occurs several (n_γ) times:

$$\vec{\chi} = \sum_\gamma \vec{\chi}^\gamma \cdot n_\gamma \quad (2.2)$$

From equations 2.1 and 2.2 follows

$$n_\gamma = \langle \chi^\gamma | \chi \rangle / g = 1/g \cdot \sum_k \chi^\gamma(\mathcal{K}) \cdot \chi(\mathcal{K}) \cdot n_k \quad (2.3)$$

With this important formula we can determine, which types and numbers of eigenstates exist in electronic (orbitals, state function) and nuclear systems (normal vibrations).

Example: Given a system with C_{3v} symmetry (e.g. PH_3), the group consists of (E), (C_3, C_3^2) = $2C_3$, ($\sigma'_v, \sigma''_v, \sigma'''_v$) = $3\sigma_v$. As basis we choose the z-shifts of the 4 nuclei, or 4-atomic s-valence orbitals. The 4×4 -matrix representation of the symmetry group operators is:

$$D : \begin{array}{c|ccc|ccc|ccc|ccc|ccc|ccc} & \mathbf{E} & & & \mathbf{C}_3 & & & \mathbf{C}_3^2 & & & \sigma'_v & & & \sigma''_v & & & \sigma'''_v & & & \\ \hline & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & \\ \hline & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & \\ \hline & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & \\ \hline & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & \end{array}$$

$$\chi : \quad 4 \quad \quad 1 \quad \quad 1 \quad \quad 2 \quad \quad 2 \quad \quad 2$$

Short version of the character vector: $\vec{\chi} = (4, 1, 2)$. We transform to the "symmetry

adapted" basis with the help of the transformation matrix $T = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{3} & 0 & 2/\sqrt{6} \\ 0 & 1/\sqrt{3} & 1/\sqrt{2} & -1/\sqrt{6} \\ 0 & 1/\sqrt{3} & -1/\sqrt{2} & -1/\sqrt{6} \end{pmatrix}$.

The transformed matrix representation is

$$D^T : \begin{array}{c|ccc|ccc|ccc|ccc|ccc|ccc} \hline & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & \\ \hline & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & \\ \hline & 0 & 0 & 1 & 0 & 0 & 0 & -1/2 & +\sqrt{3}/2 & 0 & 0 & -1/2 & -\sqrt{3}/2 & 0 & 0 & 1/2 & \sqrt{3}/2 & 0 & 0 & -1/2 & -\sqrt{3}/2 \\ \hline & 0 & 0 & 0 & 1 & 0 & 0 & -\sqrt{3}/2 & -1/2 & 0 & 0 & \sqrt{3}/2 & -1/2 & 0 & 0 & \sqrt{3}/2 & -1/2 & 0 & 0 & -\sqrt{3}/2 & 1/2 \end{array}$$

$$\chi : \quad 4=1+1+2 \quad \quad 1=1+1-1 \quad \quad 1=1+1-1 \quad \quad 2=1+1+0 \quad \quad 2=1+1+0 \quad \quad 2=1+1+0$$

With the above given transformation trick, we have "reduced" the 4-dimensional reducible representation into its irreducible components: $\chi = A_1 + A_1 + E = 2A_1 + E$

Applying eq. (2.3) we obtain (Note: the n_γ must be 0,1,2,...):

C_{3v}	$1 \cdot E$	$2 \cdot C_3$	$3 \cdot \sigma_v$	$g=6$
A_1	1	1	1	
A_2	1	1	-1	
E	2	-1	0	
χ	4	1	2	$2A_1 + E$

A_1	$1 \cdot 4$	$+1 \cdot 2 \cdot 1$	$+1 \cdot 3 \cdot 2$	$12/6=2$
A_2	$1 \cdot 4$	$+1 \cdot 2 \cdot 1$	$-1 \cdot 3 \cdot 2$	0
E	$2 \cdot 4$	$-1 \cdot 2 \cdot 1$	$+0 \cdot 3 \cdot 2$	$6/6=1$

2.3 Group Character Tables

Point Symmetry Group:

Schoenflies-symbol

Hermann-Mauguin-symbol

Equivalence Classes of symmetry operations

Irreducible Representations = Species = Rasse

A, Σ, S - one-dimensional, +1 for C_n

B - one-dimensional, -1 for C_n

$E, \Pi, \Delta, \Phi, \dots$ - two-dimensional

T, P - three-dimensional

G - four-dimensional

H, D - five-dimensional

g, u - gerade/ungerade for i (!!)

1, 2 - +1 or -1 for σ_v (not unique, if σ_v and σ_d)

Character = sum of values (trace) concerning a symmetry transformation (of a given class) of degenerate eigenvectors into itself.

Examples for the species: translation or dipole operators; rotation operators; quadruple operators.

$D_{nd} (n = 2, 3)$

$D_{2d} = V_d$
($\bar{4}2m$)

	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	$x^2 - y^2$
B_1	1	-1	1	1	-1	z	xy
B_2	1	-1	1	-1	1	(x, y)	(xz, yz)
E	2	0	-2	0	0	(R_x, R_y)	

D_{3d}
($\bar{3}m$)

	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$	
A_{1g}	1	1	1	1	1	1	$x^2 + y^2, z^2$
A_{2g}	1	1	-1	1	1	-1	R_z
E_g	2	-1	0	2	-1	0	(R_x, R_y) $(x^2 - y^2, xy)$ (xz, yz)
A_{1u}	1	1	1	-1	-1	-1	
A_{2u}	1	1	-1	-1	-1	1	z
E_u	2	-1	0	-2	1	0	(x, y)

C_{nv} ($n = 2, 3, 4, 5, 6, \infty$)

C_{2v} ($2mm$)	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

C_{3v} ($3m$)	E	$2C_3$	$3\sigma_v$			
A_1	1	1	1	z		$x^2 + y^2, z^2$
A_2	1	1	-1	R_z		
E	2	-1	0	$(x, y)(R_x, R_y)$		$(x^2 - y^2, xy)(xz, yz)$

C_{4v} ($4mm$)	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$		
A_1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	R_z	
E_1	2	$2 \cos 72^\circ$	$2 \cos 144^\circ$	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	$2 \cos 144^\circ$	$2 \cos 72^\circ$	0		$(x^2 - y^2, xy)$

C_{6v} ($6mm$)	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$		
A_1	1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	-1		
B_2	1	-1	1	-1	-1	1		
E_1	2	1	-1	-2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)
E_2	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$

$C_{\infty v}$	E	$2C_\infty^\phi$	\dots	$\infty\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	\dots	1	z	$x^2 + y^2, z^2$
$A_2 \equiv \Sigma^-$	1	1	\dots	-1	R_z	
$E_1 \equiv \Pi$	2	$2 \cos \phi$	\dots	0	$(x, y)(R_x, R_y)$	(xz, yz)
$E_2 \equiv \Delta$	2	$2 \cos 2\phi$	\dots	0		$(x^2 - y^2, xy)$
$E_3 \equiv \Phi$	2	$2 \cos 3\phi$	\dots	0		
\dots	\dots	\dots	\dots	\dots		

$C_{nh} (n = 2, 3, 4)$

C_{2h} (2/m)	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

C_{3h} (6)	E	C_3	C_3^2	σ_h	S_3	S_3^5		$\epsilon = \exp(2\pi i/3)$
A'	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
E'	$\begin{pmatrix} 1 & \epsilon & \epsilon^2 \\ 1 & \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon & \epsilon^2 \\ \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon^2 & \epsilon \\ \epsilon & \epsilon^2 \end{pmatrix}$	1	ϵ	ϵ^2	(x, y)	$(x^2 - y^2, xy)$
A''	1	1	1	-1	-1	-1	z	
E''	$\begin{pmatrix} 1 & \epsilon & \epsilon^2 \\ 1 & \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon & \epsilon^2 \\ \epsilon^2 & \epsilon \end{pmatrix}$	$\begin{pmatrix} \epsilon^2 & \epsilon \\ \epsilon & \epsilon^2 \end{pmatrix}$	-1	$-\epsilon$	$-\epsilon^2$	(R_x, R_y)	(xz, yz)

C_{4h} (4/m)	E	C_4	C_2	C_4^3	i	S_4^2	σ_h	S_4		
A_g	1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
B_g	1	-1	1	-1	1	-1	1	-1		$x^2 - y^2, xy$
E_g	$\begin{pmatrix} 1 & i & -1 & -i \\ 1 & -i & -1 & i \end{pmatrix}$	$\begin{pmatrix} -i & i \\ i & -i \end{pmatrix}$	$\begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix}$	$\begin{pmatrix} -i & i \\ i & -i \end{pmatrix}$	1	-1	-1	i	(R_x, R_y)	(xz, yz)
A_u	1	1	1	1	-1	-1	-1	-1	z	
B_u	1	-1	1	-1	-1	1	-1	1		
E_u	$\begin{pmatrix} 1 & i & -1 & -i \\ 1 & -i & -1 & i \end{pmatrix}$	$\begin{pmatrix} -i & i \\ i & -i \end{pmatrix}$	$\begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix}$	$\begin{pmatrix} -i & i \\ i & -i \end{pmatrix}$	-1	1	1	i	(x, y)	

 $D_n (n = 2, 3, 4)$

D_2 (222)	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A	1	1	1	1		x^2, y^2, z^2
B_1	1	1	-1	-1	z, R_z	xy
B_2	1	-1	1	-1	y, R_y	xz
B_3	1	-1	-1	1	x, R_x	yz

D_3 (32)	E	$2C_3$	$3C_2$		
A_1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	-1	z, R_z	
E	2	-1	0	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

D_4 (422)	E	$2C_4$	$C_2(=C_4^2)$	$2C_2'$	$2C_2''$	
A_1	1	1	1	1	1	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	z, R_z
B_1	1	-1	1	1	-1	$x^2 - y^2$
B_2	1	-1	1	-1	1	xy
E	2	0	-2	0	0	$(x, y)(R_x, R_y)$ (xz, yz)

Cubic Groups

T_d ($\bar{4}3m$)	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2,$ $x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

O_h ($m\bar{3}m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($=C_4^2$)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	$(2z^2 - x^2 - y^2,$ $x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ	$\eta^\pm = \frac{1}{2}(1 \pm 5^{1/2})$
A_g	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
T_{1g}	3	η^+	η^-	0	-1	3	η^-	η^+	0	-1	(R_x, R_y, R_z)
T_{2g}	3	η^-	η^+	0	-1	3	η^+	η^-	0	-1	
G_g	4	-1	-1	1	0	4	-1	-1	1	0	
H_g	5	0	0	-1	1	5	0	0	-1	1	$(2z^2 - x^2 - y^2,$ $x^2 - y^2,$ $xy, yz, zx)$
A_u	1	1	1	1	1	-1	-1	-1	-1	-1	
T_{1u}	3	η^+	η^-	0	-1	-3	$-\eta^-$	$-\eta^+$	0	1	(x, y, z)
T_{2u}	3	η^-	η^+	0	-1	-3	$-\eta^+$	$-\eta^-$	0	1	
G_u	4	-1	-1	1	0	-4	1	1	-1	0	
H_u	5	0	0	-1	1	-5	0	0	1	-1	

3 Nuclear Vibrations


3.1 Normal vibrations

The motions or distributions of nuclei (atoms) in molecules with N atoms is described classically or quantum mechanically with the help of the respective 3N cartesian coordinates. One can construct 3N linear independent linear combinations of the original coordinates, which correspond to the 3 overall translations of the whole molecule in x, y, z -direction; to 3 overall rotations of the molecule around the 3 "main axes", which are equivalent to the set of rotations around the 3 cartesian axes, R_x, R_y, R_z . In the case of a linear molecule, the rotation around the molecular axis is not a nuclear rotation, but a rotation of the electric shell (rotation of a nucleus around its own axis would mean another radioactive (γ) nuclear state of extremely high energy). So there are 3N-6 or -5 nuclear motions: vibrations, and possibly internal rotations, librations or other large amplitude motions. Concerning comparably rigid molecules at comparably low energies, the 3N-6 or -5 internal motions are symmetry-adapted, uncoupled, so-called "normal vibrations". They are determined through the coupling of individual bond variations. Here are two simple examples:

3.2 Quadratic forms

1) H₂O bond stretches:

The potential energy varies approximately as $E = k/2 \cdot (\Delta R_1^2 + \Delta R_2^2) + \kappa \cdot \Delta R_1 \cdot \Delta R_2$ in terms of (mass-weighted) internal coordinates ΔR_i . This quadratic form can be written as

$$E = 1/2 \cdot \langle \Delta R_1, \Delta R_2 | \begin{bmatrix} k & \kappa \\ \kappa & k \end{bmatrix} | \begin{matrix} \Delta R_1 \\ \Delta R_2 \end{matrix} \rangle = 1/2 \cdot \langle \nu_1, \nu_2 | \begin{bmatrix} k + \kappa & 0 \\ 0 & k - \kappa \end{bmatrix} | \begin{matrix} \nu_1 \\ \nu_2 \end{matrix} \rangle$$


$k \pm \kappa$ are the eigenvalues of the force constants matrix, and ν_i are the eigenvectors, the "normal" coordinates $\nu_1 = (\Delta R_1 + \Delta R_2)/\sqrt{2}$, $\nu_2 = (\Delta R_1 - \Delta R_2)/\sqrt{2}$



2) H₂O breathing and bending:

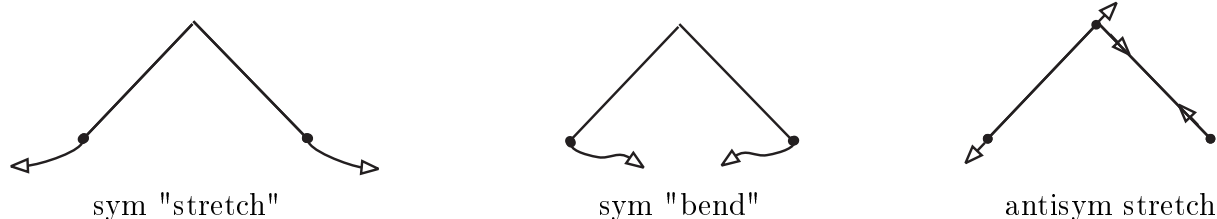
$$E = 1/2 \cdot k_{br} \cdot (\nu_1)^2 + 1/2 \cdot k_{bd} \cdot (\Delta\alpha)^2 + \gamma \cdot \nu_1 \cdot \Delta\alpha$$

$$E = 1/2 \cdot \langle \nu_1, \Delta\alpha | \begin{bmatrix} k_{br} & \gamma \\ \gamma & k_{bd} \end{bmatrix} | \begin{matrix} \nu_1 \\ \Delta\alpha \end{matrix} \rangle = 1/2 \cdot \langle \nu_+, \nu_- | \begin{bmatrix} k_+ & 0 \\ 0 & k_- \end{bmatrix} | \begin{matrix} \nu_+ \\ \nu_- \end{matrix} \rangle$$

$$\kappa_{+,-} = (k_{br} + k_{bd})/2 \pm \sqrt{(k_{br} - k_{bd})^2/4 + \gamma^2} \approx k_{br} + \gamma^2/(k_{br} + k_{bd}) \text{ or } k_{bd} - \gamma^2/(k_{br} - k_{bd}) .$$

Note: In lowest order of approximation, the motion of N atoms is described by about $4.5(N - 2)^2$ general force constants. This can be reduced to $3(N - 2)$ normal force constants.

Note: The basic independent motion types of a molecule are symmetry adapted mixtures of all possible internal motions. Example: H₂O



3.3 Symmetry Analysis

The character of symmetry operations S is independent of the directions of the motional coordinates of each atom. Therefore choose the cartesian coordinates of every atom in each case of S in the most appropriate manner.

$$\chi(S) = N_{fix} \cdot (2 \cdot \cos \phi \pm 1)$$

N_{fix} = number of nuclei not moved from their position by S ; ϕ = angle of rotation (C_1 : 0° ; C_2 : 180° ; etc; σ : 0° ; i : 180°); +1 for pure rotation, -1 for "improper" mirror rotation ($\sigma = S_1$, $i = S_2$, etc.).

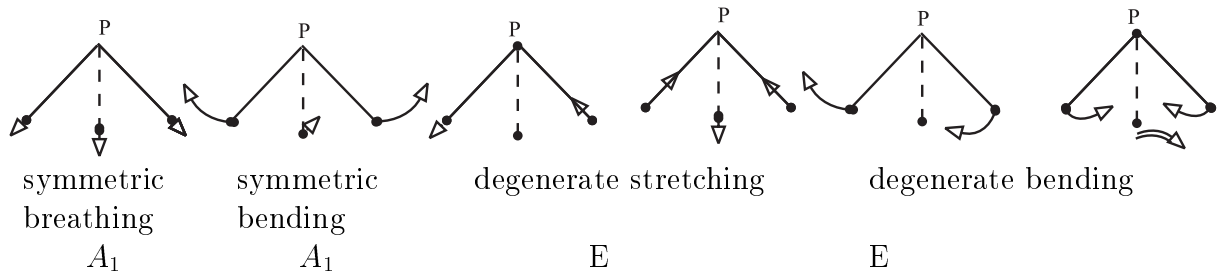
Example: PH₃

C_{3v}	E	$2C_3$	$3\sigma_v$	g=6
A_1	1	1	1	$z; x^2 + y^2; z^2$
A_2	1	1	-1	R_z
E	2	-1	0	$(x, y); (R_x, R_y); (xy, x^2 - y^2)(xz, yz)$
N_{fix}	4	1	2	
n_k	1	2	3	
ϕ	0	120°	0	
$2 \cos \phi$	2	-1	2	
± 1	+1	+1	-1	
$2 \cos \phi \pm 1$	3	0	1	
$N_{fix} \cdot n_k(2c \pm 1)$	12	0	6	
$\langle A_1 \chi \rangle$	12		+6	18:6=3
$\langle A_2 \chi \rangle$	12		-6	6:6=1
$\langle E \chi \rangle$	24		+0	24:6=4

$$4 \text{ atoms} = 12 \text{ motions} = 3A_1 + A_2 + 4E$$

Translations are $x, y, z = A_1 + E$; Rotations are $R_x, R_y, R_z = A_2 + E$

Remaining vibrations: $2A_1 + 2E$ - There are $3N-6=6$ vibrational freedoms, giving rise to 4 normal modes, two nondegenerate symmetric ones and two degenerate skew ones.



IR active vibrations (in lowest order of approximation, at low temperatures) are those of x, y, z -type: A_1, E . Raman active are those of x^2, xy etc. type: A_1, E (in this case accidentally the same as IR). In the present special example, all vibrations are detectable in both kinds of spectra.

The emission and absorption probabilities (intensities) of electromagnetic spectra [rotational excitation in the microwave (MW) region; vibrational excitation in the infrared region (IR); valence electronic absorption or fluorescence or vibrational inelastic photon scattering (Raman) in the visible and near ultraviolet region (VIS-UV); core electronic excitation in the far UV and X-ray region (X-UV)] are proportional to the value squared of the transition moment (transition matrix element):

$$\sim |\langle \psi_i | \widehat{O}_p | \psi_f \rangle|^2$$

ψ_i and ψ_f are the wave functions of the initial and final nuclear (vibrational, rotational) and electronic states of the transition. And \widehat{O}_p is the operator of interaction of the electric wave with the electronic and nuclear charges, the largest contribution usually being $\sim \sqrt{I} \cdot \vec{r} \cdot (-e \text{ or } +Ze)$ for absorption or emission, and the respective product for the absorption-emission-Raman-effect.