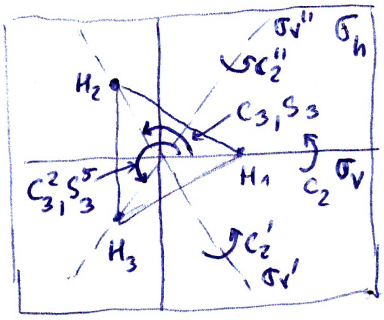
Tutorial: Character table of point groups D_{3h} and C_{3v} (T5)

- D_{3h} is the group of symmetry of the equilateral triangle which is an equilibrium geometry of the cation H_3^+ and C_{3v} (the group of symmetry of ammonia) is its subgroup

- <u>symmetry operations</u> = 12 elements of D_{3h}



- subgroup $C_{3v} = \{E, C_3, C_3^2, \sigma_v, \sigma_v', \sigma_v''\}$, where $C_3^2 = C_3^{-1}$

left coset $\sigma_h \cdot C_{3v} = \{\sigma_h, S_3, S_3^5, C_2, C_2', C_2''\}$ in D_{3h}, where $S_3^5 = S_3^{-1}$

(note that $S_3^2 = C_3^2$, $S_3^3 = \sigma_h$, $S_3^4 = C_3$ and finally $S_3^5 = \sigma_h C_3^2$ is a new element)

- <u>conjugacy classes</u> - elements that belong to one conj. class are those whose symmetry elements can be transformed to each other by some symmetry operation in the group

e.g. the rotational axis C_2 can be transformed to C_2' by C_3, S_3, C_2'' or σ_v''

	conj. class	elements	conjugation by (examples)	
C_{3v}	E	$\{E\}$	—	
	$2C_3$	$\{C_3, C_3^2\}$	σ_v or C_2	these change the direction of rotation
	$3\sigma_v$	$\{\sigma_v, \sigma_v', \sigma_v''\}$	C_3 or C_3^2	← rotation of the mirror planes
these mirror planes cannot be transformed to each other	σ_h	$\{\sigma_h\}$	—	← commutes with everything
	$2S_3$	$\{S_3, S_3^5\}$	σ_v or C_2	
	$3C_2$	$\{C_2, C_2', C_2''\}$	C_3 or C_3^2	← rotation of the axis

- <u>number and dimensions of irreducible representations (IRs)</u>
  - C_{3v} has 3 classes $\Rightarrow$ 3 IRs $\Rightarrow \sum_{\mu=1}^{3} d_\mu^2 = 6 \Rightarrow 1^2+1^2+2^2=6$ (the only possibility)
  - D_{3h} has 6 classes $\Rightarrow$ 6 IRs $\Rightarrow \sum_{\mu=1}^{6} d_\mu^2 = 12 \Rightarrow 1^2+1^2+1^2+1^2+2^2+2^2=12$ (again the only possibility)
  - dimensions are $\chi(E)$ and are in the first column of the table

- <u>trivial repr.</u> ($D(g)=1$ for all $g \in G$) $\Rightarrow$ the first row of the table

D_{3h}	E	$2C_3$	$3\sigma_v$	σ_h	$2S_3$	$3C_2$
Γ^1	1	1	1	1	1	1

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- vector representation for D_{3h} – we choose the z-axis as the main axis C_3 → we get reducible repr. as z-component is independent of x and y for all group elements
- it is enough to consider only characters (no matrices needed)

D_{3h}	E	$2C_3$	$3\sigma_v$	σ_h	$2S_3$	$3C_2$	
	$\overbrace{\qquad\qquad}^{C_{3v}}$						
vector representation → Γ^v	3	0	+1	1	−2	−1	← from $\chi^v(C_3) = 1+2\cos\frac{2\pi}{3} = 0$, $\chi^v(S_3) = -1+2\cos\frac{2\pi}{3} = -2$
Γ^z	1	1	1	−1	−1	−1	← z changes sign for σ_h; $S_3 = \sigma_h C_3$ and $C_2 = \sigma_h \cdot \sigma_v$
$\Gamma^{(x,y)}$	2	−1	0	2	−1	0	

$\chi^{(x,y)}(g) = \chi^V(g) - \chi^z(g)$ ← χ^V is the trace of 3x3 matrices and χ^z are on the diagonal, the last elem.

- using Frobenius criterion of irreducibility

$$\sum_{k=1}^{N_c} n_k \chi^*(C_k)\chi(C_k) = \#G = 12 \quad (\text{for } D_{3h})$$

we can check that Γ^V is reducible $\Sigma = 24$ but $\Gamma^{(x,y)}$ is irreducible as

$$\Sigma = 1\cdot 2^2 + 2\cdot(-1)^2 + 0 + 1\cdot 2^2 + 2\cdot(-1)^2 + 0 = 12$$

- pseudovector representation for D_{3h}
- now $\chi^{pv}(g) = \det D^v(g)\cdot\chi^v(g)$ and $\det D^v(g) =$ +1 for proper rotations, −1 for improper

thus

D_{3h}	E	$2C_3$	$3\sigma_v$	σ_h	$2S_3$	$3C_2$
Γ^{pv}	3	0	−1	−1	2	−1
Γ^{R_z}	1	1	−1	1	1	−1
$\Gamma^{(R_x,R_y)}$	2	−1	0	−2	1	0

here we just changed the signs for σ_v, σ_h, S_3 in $\Gamma^v, \Gamma^z, \Gamma^{(x,y)}$

these two (Γ^{R_z}, $\Gamma^{(R_x,R_y)}$) are again irred. repr. (check using Frob.)

- full character table – we have already 5 IRs above; the last can be obtain e.g. using orthogonality relations for columns

C_{3v} / D_{3h}	E	$2C_3$	$3\sigma_v$	σ_h	$2S_3$	$3C_2$	D_{3h}	C_{3v}	D_{3h}	C_{3v}
$A_1 = A_1' = \Gamma^1$	1	1	1	1	1	1	—	z	x^2+y^2, z^2	x^2+y^2, z^2
$A_2 = A_2' = \Gamma^{R_z}$	1	1	−1	1	1	−1	R_z	R_z	—	—
$E = E' = \Gamma^{(x,y)}$	2	−1	0	2	−1	0	(x,y)	(x,y) (R_x,R_y)	(x^2-y^2, xy)	(x^2-y^2, xy) (xz, yz)
$A_1'' = \Gamma^{\det}$	1	1	−1	−1	−1	1	—	—	—	—
$A_2'' = \Gamma^z$	1	1	1	−1	−1	−1	z	—	—	—
$E'' = \Gamma^{(R_x,R_y)}$	2	−1	0	−2	1	0	(R_x,R_y)	—	(xz, yz)	—

this last IR is the antisymmetric repr. with $\chi(g) = \det D^v(g)$

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Labels / Symbols of IRs for point groups

- one-dimensional IRs: A if $\chi(C_n) = +1$, B if $\chi(C_n) = -1$ } main axis

further we use A' or A'' if $\chi(\sigma_h) = \pm 1$

A_g or A_u if $\chi(i) = \pm 1$ gerade / ungerade

and $A_1, A_2, \dots$ or $B_1, B_2, \dots$ if we cannot use anything above or there are more 1-dim. IRs that cannot be distinguish by rules above

Examples:

$H_2O \to$

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

B

no σ_h or i

D_2	E	$C_2(z)$	$C_2'(y)$	$C_2''(x)$
A	1	1	1	1
B_1	1	1	-1	-1
B_2	1	-1	1	-1
B_3	1	-1	-1	1

changes of signs

it is not clear which axis is the main one

- two-dimensional IRs: E
  - including „real" 2-dim. repr. for cyclic groups which are combinations of two 1-dim complex IRs

- 3D: T, 4D: G, 5D: H

- indices g, u, 1, 2, 3, and prime ' or double prime " are used in a similar way as for A or B

Example:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-2	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

σ_d is not σ_h => no A' or A''

S_4 is not C_4 => no B

but for T_h group which has i as one element we set A_g, E_g, T_g and A_u, E_u, T_u

- special symbols are used for $C_{\infty v}$ and $D_{\infty h}$

$C_{\infty v}$: $A_1 = \Sigma^+$, $A_2 = \Sigma^-$, $E_1 = \Pi$, $E_2 = \Delta$ etc.

$D_{\infty h}$: $A_{1g} = \Sigma_g^+$, $A_{2g} = \Sigma_g^-$, $E_{1g} = \Pi_g$ etc.

similarly for Ungerade

(as s, p, d, f for H)

$\Sigma, \Pi, \Delta, \Phi$

according to the projection of orbital momentum $|L_z| = 0, 1, 2, 3, \dots$