Group theory and molecular vibrations

We consider ammonia NH_3.

Point group C_{3v}

Possible operations are

	E	C_3	C_3^2	σ_v^a	σ_v^b	σ_v^c
E	E	C_3	C_3^2	σ_v^a	σ_v^b	σ_v^c
C_3	C_3	C_3^2	E	σ_v^c	σ_v^a	σ_v^b
C_3^2	C_3^2	E	C_3	σ_v^b	σ_v^c	σ_v^a
σ_v^a	σ_v^a	σ_v^b	σ_v^c	E	C_3	C_3^2
σ_v^b	σ_v^b	σ_v^c	σ_v^a	C_3^2	E	C_3
σ_v^c	σ_v^c	σ_v^a	σ_v^b	C_3	C_3^2	E

This is called Cayley table.

Why this is useful?

Every symmetry operation is some transformation of atomic coordinates in a molecule.

It is an operator which can be represented in some way, for example by matrix.

Example: Rotation matrix

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

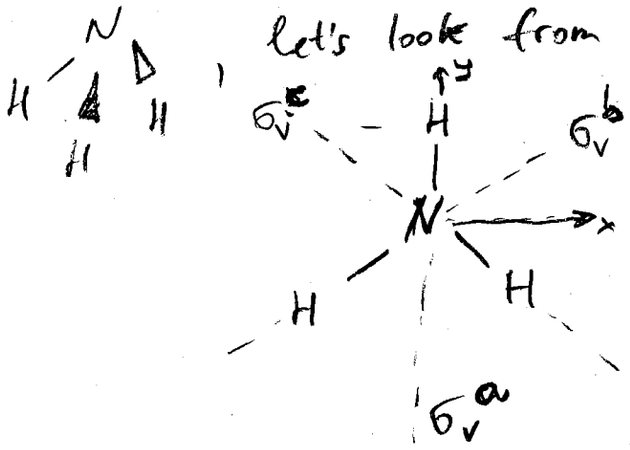
One can write set of matrix for every symmetry operation in the group.

If all the operation are represented somehow and they obey Cayley table, we call this set <u>a representation of a group.</u>

Representation depends on how we represent atomic coordinates, what is the coordinate origin etc.

⇒ Therefore, number of representations is <u>infinite.</u>

Let's try to express some representation for C_{3v} group of ammonia:



Let's choose coordinate system with N in a center of coordinates, so we don't care about it.

How H atoms transform under C_3, C_3^2, and various σ_v ?

Let's use 2x2 matrices and write all symmetry operations of the group:

$$E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \text{ - trivial}$$

$$C_3 = \begin{pmatrix} \cos\frac{2\pi}{3} & -\sin\frac{2\pi}{3} \\ \sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$C_3^2 = \begin{pmatrix} \cos\left(\frac{2\pi}{3}2\right) & -\sin\left(\frac{2\pi}{3}2\right) \\ \sin\left(\frac{2\pi}{3}\cdot 2\right) & \cos\left(\frac{2\pi}{3}\cdot 2\right) \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

Reflections can also be written easily:

Positions of Hydrogens in our choosen coordinate system:

$$H_1 = \begin{pmatrix} 0 \\ a \end{pmatrix} \qquad H_2 = \begin{pmatrix} \cos(30^\circ) \\ -\sin(30^\circ) \end{pmatrix} = \begin{pmatrix} \sqrt{3}/2 \\ -\frac{1}{2} \end{pmatrix}$$

$$H_3 = \begin{pmatrix} -\sqrt{3}/2 \\ -\frac{1}{2} \end{pmatrix}$$

One can show that σ_v matrices can be expressed as:

$$\sigma_v^a = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \sigma_v^b = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$\sigma_v^c = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

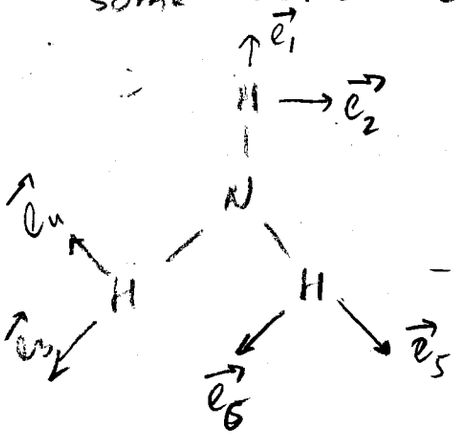
The set of matrices we found is one of the representations of the group C_{3v}.

Can we find some other representations which obey Cayley table? Yes! even some trivial ones:

Representations (let's denote it by Γ letters)	E	C_3	C_3^2	σ_v^a	σ_v^b	σ_v^c
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	-1	-1	-1
Γ_3	—— " —— " —— our 2×2 representation —" —					
⋮	etc. infinite number!					

However, representations can be classified in two classes which we discuss now:

As an example for ammonia let's choose some weird coordinate system:



Let's represent some of the symmetry operations in the chosen basis:

$$C_3 = \begin{pmatrix} & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \end{pmatrix} \begin{pmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{pmatrix} = \begin{pmatrix} e_3 \\ e_4 \\ e_5 \\ e_6 \\ e_1 \\ e_2 \end{pmatrix}$$

The matrix is

$$C_3 = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix}$$

similarly, we can construct other symmetry operations in some representation Γ_4.

What is special about Γ_4 representation?

One can prove, that

$\Gamma_4(C_3)$ can be written as

$$\Gamma_4'(C_3) = \Theta^{-1}\,\Gamma_4(C_3)\,\Theta = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

One can recognize that

$\Gamma_4'(C_3)$ is composed from <u>other representations</u>:

$$\Gamma_4'(C_3) = \begin{pmatrix} \Gamma_1(C_3) & & 0 & \\ & \Gamma_2(C_3) & & \\ 0 & & \Gamma_3(C_3) & \\ & & & \Gamma_3(C_3) \end{pmatrix}$$

Therefore Γ_4 can be <u>reduced</u> to other (↑ a set of) representations $\Gamma_1, \Gamma_2, \Gamma_3$.

We call Γ_4 representation <u>reducible</u> if exists such a transformation Θ that block-diagonalizes <u>all</u> the symmetry operations of the group.

Such representations are <u>reducible</u>. Those which cannot be reduced – <u>irreducible</u>.

How to decompose reducible repr. to a set of irreducible in a general case?

What is important about matrices is that they conserve <u>trace</u> under similarity transformations such as rotations etc. Therefore, instead of operating with matrices when we decompose reducible repr. to irrep, we can use traces.

The trace of symmetry operation in a given representation is called <u>character</u>.

We can constant characters table of a group.

C_{3v}	E	C_3	C_3^2	σ_v^a	σ_v^b	σ_v^c
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	−1	−1	−1
Γ_3	2	−1	−1	0	0	0

or more compact version

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

Mulliken symbols.

A, B - one dimensional rep.

E - two dimensional

T - three dimens.

Let's try to use characters table to classify 1) symmetry operations
2) possible motions in a molecule

Let's use Cartesian coordinates for simplicity:

1) $\hat{E} = \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix}$ } $3K$, therefor $tr(\hat{E}) = 3K$

2) Reflections $\hat{\sigma} = \begin{pmatrix} 1 & & \\ & 1 & \\ & & -1 \end{pmatrix}$ in the plane xOy, i.e. with respect to z axis.

$tr(\hat{\sigma}) = N_\sigma$ – atoms located at reflection plane

3) Rotations

$$\hat{C} = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad tr(\hat{C}) = N_C(1 + 2\cos\theta)$$

N_C: number of atoms staying on the rotational axis.

	E	σ	C_θ	i	S_θ
Γ	$3K$	N_σ	$N_C(1+2\cos\theta)$	...	...

The arbitrary motion Γ can be decomposed

1) $\Gamma = \Gamma_{tr} \oplus \Gamma_{rot} \oplus \Gamma_{vib}$

2) $\Gamma_{vib} = \Gamma_1 \oplus \Gamma_2 \oplus \ldots$

Let's do it for the case of ammonia.

	E	3σ	$2C_\theta$
Γ_{vib}	$3N-6$	N_σ	$N_c(1+2\cos\theta)$
	$\parallel$	$\parallel$	$\parallel$
	6	2	$\frac{2\pi}{3}$
	(two atoms out of plane)		$\parallel$
			0, because $\cos\frac{2\pi}{3} = -\frac{1}{2}$

thus we have

	E	3σ	$2C_3$
Γ_{vib}	6	2	0

and we want to expand this in a basis of irreducible representations:

C_{3v}	E	3σ	$2C_3$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

in fact we need to solve

$$a A_1 + b A_2 + c E = \Gamma_{vib}$$

for ammonia we find

$$\boxed{\Gamma_{vib} = 2A_1 \oplus 2E}$$

$2A_1$: fully symmetric vibrations

$2E$: two pairs (4 in total) doubly degenerate vibrations transforming according to E representation