MOLECULAR VIBRATIONS AND GROUP THEORY

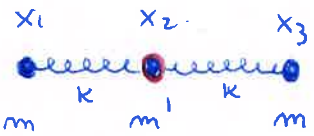
We consider a system of point masses held together by forces which keep the system rather rigid. We assume that we know the number of masses but not the shape of the system at equilibrium. We can shake the system and study its vibration modes. We want to show how to use group theory to determine the "shape" of the molecule at equilibrium.

Let $\underline{q}$ be the vector describing the deviations of the system from equilibrium. If we have N atoms, we will have a vector with 3N components. If we have small oscillations around the equilibrium, we will have an equation of the form

$$\ddot{\underline{q}} = -F\underline{q}$$

The eigenvalues of the matrix F determine the oscillation frequencies.

Suppose that our molecule consists of 3 atoms, one of mass m' and two of mass m



$$\underline{q} = \begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix}$$

example CO_2 !

For example, we can have $x_1 = q_1$, $x_2 = x_0 + q_2$, $x_3 = 2x_0 + q_3$

Newton's law tells us that

$$\begin{cases} m\ddot{q}_1 = k(q_2 - q_1) \\ m'\ddot{q}_2 = k(q_3 - q_2) - k(q_2 - q_1) \\ m\ddot{q}_3 = -k(q_3 - q_2) \end{cases}$$

This means that F has the following form

$$F = \frac{k}{m}\begin{pmatrix} 1 & -1 & 0 \\ -e & +2e & -e \\ 0 & -1 & 1 \end{pmatrix} \qquad e = \frac{m}{m'}$$

The eigenvalues and eigenvectors of F give the normal modes of the system.

EIGENVALUE	EIGENVECTOR	MODE
0	$\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$	uniform translation
$\frac{k}{m}$	$\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$	symmetric stretching
$\frac{k}{m}(1+2e)$	$\begin{pmatrix} -1 \\ 2e \\ -1 \end{pmatrix}$	asymmetric stretching

If the molecule possesses some symmetry under a group G, then G acts on the space V of displacements. If G is a symmetry, the operator F must commute with the action of G. In our example G includes the exchange of 1 and 3, which is realised by the matrix

$$A = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \qquad [A, F] = 0$$

We thus have a representation of G on V and an operator F which commutes with it.

Suppose that the representation is irreducible

$\Rightarrow$ Schur's lemma would tell us that F is a multiple of the identity, that is, it has only one eigenvalue

In general, however, the number of eigenvalues of the operator F should be equal to the dimension of space. We can now argue backwards:

If we observe only one frequency, we conclude that there must be a group G which acts through an irreducible representation. More generally, suppose that we have a candidate symmetry group for our molecule whose action on the space V breaks down into four irreducible reps.

$$U = U_1 \oplus U_2 \oplus U_3 \oplus U_4$$

If we observe four frequencies, we have evidence that the symmetry group could indeed be the correct one

$\Rightarrow$ MOLECULAR SPECTROSCOPY AS APPLICATION OF THE SCHUR'S LEMMA!

But what happens in our example?

The relevant group is $C_2 = \{E, A\}$ $\quad E = \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix} \quad A = \begin{pmatrix} & & 1 \\ & 1 & \\ 1 & & \end{pmatrix}$

The symmetry is realized with a 3 dimensional, reducible representation

The character table of C_2 is

	e	a
1	1	1
2	1	-1

or

$$\tilde{\chi}_1 = \left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \right)$$

$$\tilde{\chi}_2 = \left(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}} \right)$$

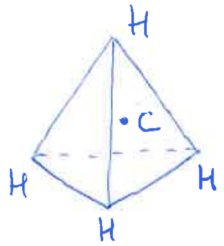
For our representation we have $\tilde{\chi} = \left(\frac{3}{\sqrt{2}} , \frac{1}{\sqrt{2}} \right)$

$\Rightarrow$ $m_1 = \tilde{\chi} \cdot \tilde{\chi}_1 = 2$

$m_2 = 1$ $\Rightarrow$ $U = 2U_1 \oplus U_2$ $\Rightarrow$ 3 modes!

Subtracting one frequency for the rigid translation we get 2 vibrational frequencies!

THE CASE OF CH_4



We now want to discuss the case of the methane molecule CH_4, which has a tetrahedral symmetry.

The potential energy is a function of the four coordinates of the H atoms + those of the C atom $\Rightarrow$ we have $3 \times 5 = 15$ dimensions.

We consider small perturbations around the equilibrium position and we try to predict the frequencies from symmetry considerations and group theory.

The symmetries are

$$V(R\underline{x}_1, R\underline{x}_2, R\underline{x}_3, R\underline{x}_4, R\underline{x}_c) = V(\underline{x}_1, \underline{x}_2, \underline{x}_3, \underline{x}_c) \qquad R \in O(3) \text{ rotation}$$

$$V(\underline{x}_{\sigma(1)}, \underline{x}_{\sigma(2)}, \underline{x}_{\sigma(3)}, \underline{x}_{\sigma(4)}, \underline{x}_c) = V(\underline{x}_1, \underline{x}_2, \underline{x}_3, \underline{x}_c) \qquad \sigma \in S_4$$

The tetrahedral group T (symmetry group of a regular tetrahedron) is isomorphic to S_4

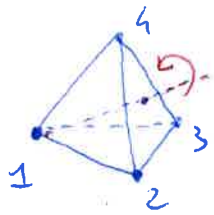
S_4 has 5 classes and thus 5 irreducible representations. To construct them we can exploit the fact that $H = \{ e, (12)(34), (13)(24), (14)(23) \}$ is an invariant subgroup and that $S_4 / H \sim S_3$.

We now describe the group elements of T and their correspondence with S_4

e identity [1]

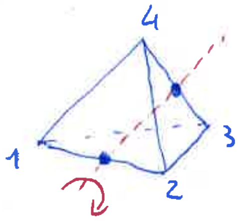
2×4 =

r_3 rotations around an axis through a vertex [8] by $2/3\,\pi$



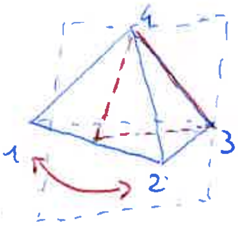
3→4
4→2
2→3

r_2 half turn around a line joining two sides through their midpoints [3]



1↔2
3↔4

τ reflection [6] around the plane between two vertices and the mid point of opposite side



1↔2

s_4 composition of r_3 and τ [6]

The elements of the group can also be represented by using the S_4 notation

e (·)(·)(·)(·) 1-cycle

r_3 (· · ·) 3-cycle

r_2 (· ·)(· ·) 2-2cycles

τ (· ·) 2-cycle

s_4 (· · · ·) 4-cycle

For example

$$(234)\circ(12) = \begin{pmatrix}1\,2\,3\,4\\1\,3\,4\,2\end{pmatrix}\circ\begin{pmatrix}1\,2\,3\,4\\2\,1\,3\,4\end{pmatrix} = \begin{pmatrix}1\,2\,3\,4\\3\,1\,4\,2\end{pmatrix} = (1342)$$

The problem we have is to decompose the 15 dimensional representation into irreducible representations.

The character table of S_4 is

$24\,S_4$	e	$8[\tau_3]$	$3[\tau_2]$	$6[\sigma_4]$	$6[\tau]$
1	1	1	1	1	1
2	2	-1	2	0	0
3	1	1	1	-1	-1
4	3	0	-1	1	-1
5	3	0	-1	-1	1

normalized characters

$$\tilde{\chi}_1 = \left(\frac{1}{\sqrt{24}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{8}}, \frac{1}{2}, \frac{1}{2}\right)$$

$$\tilde{\chi}_2 = \left(\frac{2}{\sqrt{24}}, -\frac{1}{\sqrt{3}}, \frac{2}{\sqrt{8}}, 0, 0\right)$$

$$\tilde{\chi}_3 = \left(\frac{1}{\sqrt{24}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{8}}, -\frac{1}{2}, -\frac{1}{2}\right)$$

$$\tilde{\chi}_4 = \left(\frac{3}{\sqrt{24}}, 0, -\frac{1}{\sqrt{8}}, \frac{1}{2}, -\frac{1}{2}\right)$$

$$\tilde{\chi}_5 = \left(\frac{3}{\sqrt{24}}, 0, -\frac{1}{\sqrt{8}}, -\frac{1}{2}, \frac{1}{2}\right)$$

To project out our 15-dimensional representation on the 5 irreducible reps we have to compute χ_U

For example, consider $\tau = (34)$. The corresponding matrix $U(R)$ is

$$U(R) = \begin{array}{c} \begin{pmatrix} R & & & & \\ & R & & & \\ & & 0 & R & \\ & & R & 0 & \\ & & & & R \end{pmatrix} \end{array} \begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{array}$$

we get $\chi_U = 3\,\mathrm{Tr}\,R$
$\uparrow$ number of fixed points

This result is general: the character is given by the relation $\chi_U(R) = N_R\,\mathrm{Tr}(R)$
\# fixed points

$\Rightarrow$ we have to compute $\mathrm{Tr}(R)$!

A rotation of angle ϑ can be represented as
$$\begin{pmatrix} \cos\vartheta & \sin\vartheta & 0 \\ -\sin\vartheta & \cos\vartheta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$\Rightarrow \mathrm{Tr}(\tau_3) = 0$ and $\mathrm{tr}(\tau_2) = -1$

A reflection can be represented as $\begin{pmatrix} 1 & & \\ & 1 & \\ & & -1 \end{pmatrix} \Rightarrow \mathrm{tr}(\tau) = 1$.

One can show that $\mathrm{tr}(\sigma_4) = -1$

We can thus compute all the characters for U

We obtain

$\chi_U(e) = 15$ $\chi_U(r_3) = 0$ $\chi_U(r_2) = -1 \cdot 1$

only the C atom is fixed

$\chi_U(s_4) = -1 \cdot 1 = -1$ $\chi_U(\tau) = 1 \cdot 3$

(2H + C atoms fixed)

We thus have

$$\chi_U = \begin{array}{c} \\ \end{array}\!\!\left(\overset{e}{15}, \overset{r_3}{0}, \overset{r_2}{-1}, \overset{s_4}{-1}, \overset{\tau}{3}\right) \quad \text{and} \quad \tilde{\chi}_U = \left(\frac{15}{\sqrt{24}}, 0, -\frac{1}{\sqrt{8}}, -\frac{1}{2}, \frac{3}{2}\right)$$

By using the formula $m_\mu = \tilde{\chi} \cdot \tilde{\chi}_\mu^+$ we obtain

$m_1 = 1$ $m_2 = 1$ $m_3 = 0$ $m_4 = 1$ $m_5 = 3$

$$\Rightarrow \quad U = \overset{1}{U_1} \oplus \overset{2}{U_2} \oplus \overset{3}{U_4} \oplus \overset{3}{U_5} \oplus \overset{3}{U_5} \oplus \overset{3}{U_5} \quad = 15 \checkmark$$

We expect at most 6 frequencies!

One can show that there are 2 3-dim eigenspaces (corresponding to U_4 and U_5)

that correspond to rigid rotations and traslations

$\Rightarrow$ ONLY 4 FREQUENCIES $U \sim U_1 + U_2 + 2U_5$

1 dim: BREATHING

2 dim

3 dim