

An aerial, top-down view of a city street, likely in New York City, showing tall apartment buildings on either side of a multi-lane road. A large, semi-transparent yellow arrow is superimposed over the center of the image, pointing both left and right. The text 'GROUP THEORY' is written in large, bold, yellow, serif capital letters across the top half of the image. The word 'in' is written in a smaller, yellow, cursive script at the bottom right corner.

**GROUP  
THEORY**

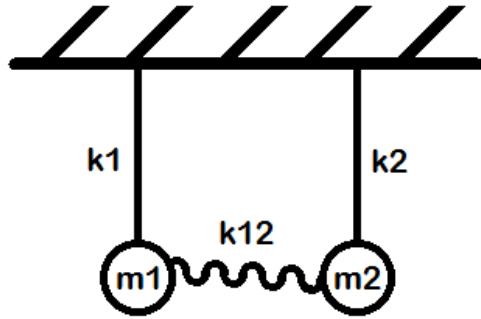
*in*

# Molecular Vibration

[illegible]

EXPERIENCE IT **JULY 16** IN THEATERS AND **IMAX**

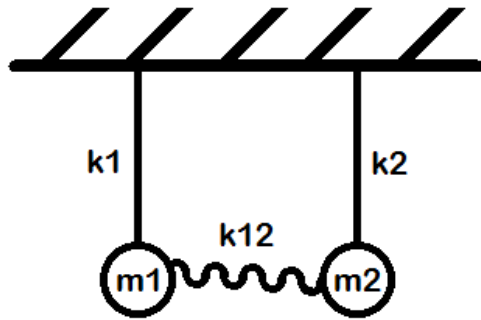
# Solving Vibrational Problems... So easy!!



Normal Modes

$$q = \vec{q}(t) = c \vec{\xi} e^{-i\omega t}$$

# Solving Vibrational Problems... So easy!!

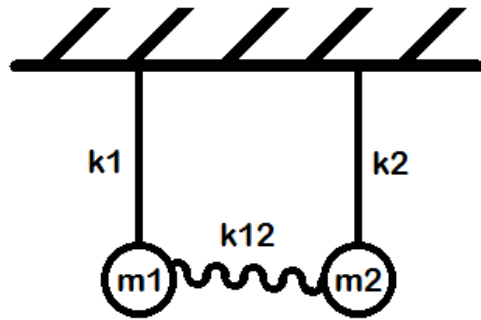


Normal Modes

$$q = \vec{q}(t) = c \vec{\xi} e^{-i\omega t}$$

eigenvectors      frequencies

# Solving Vibrational Problems... So easy!!



Normal Modes

$$q = \vec{q}(t) = c \vec{\xi} e^{-i\omega t}$$

Quadratic Lagrangian

$$\mathcal{L} = \frac{1}{2} [\dot{q}^T M \dot{q} - q^T V q]$$

Equations of Motion

$$\begin{aligned} M\ddot{q} + Vq &= 0 \\ (V - \omega^2 M)q &= 0 \\ \det(V - \omega^2 M) &= 0 \end{aligned}$$

Equations of Motion

$$\begin{aligned} M\ddot{q} + Vq &= 0 \\ \ddot{q} + \tilde{V}q &= 0 \\ \tilde{V}\xi &= \omega^2 \xi \end{aligned}$$

Linearized Potential

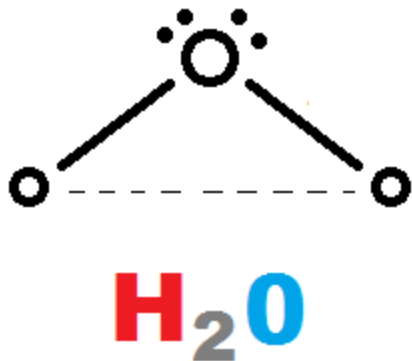
$$V_{ij} = \frac{\partial^2 V}{\partial x_j \partial x_i}$$

about a (quasi-)stable  
equilibrium

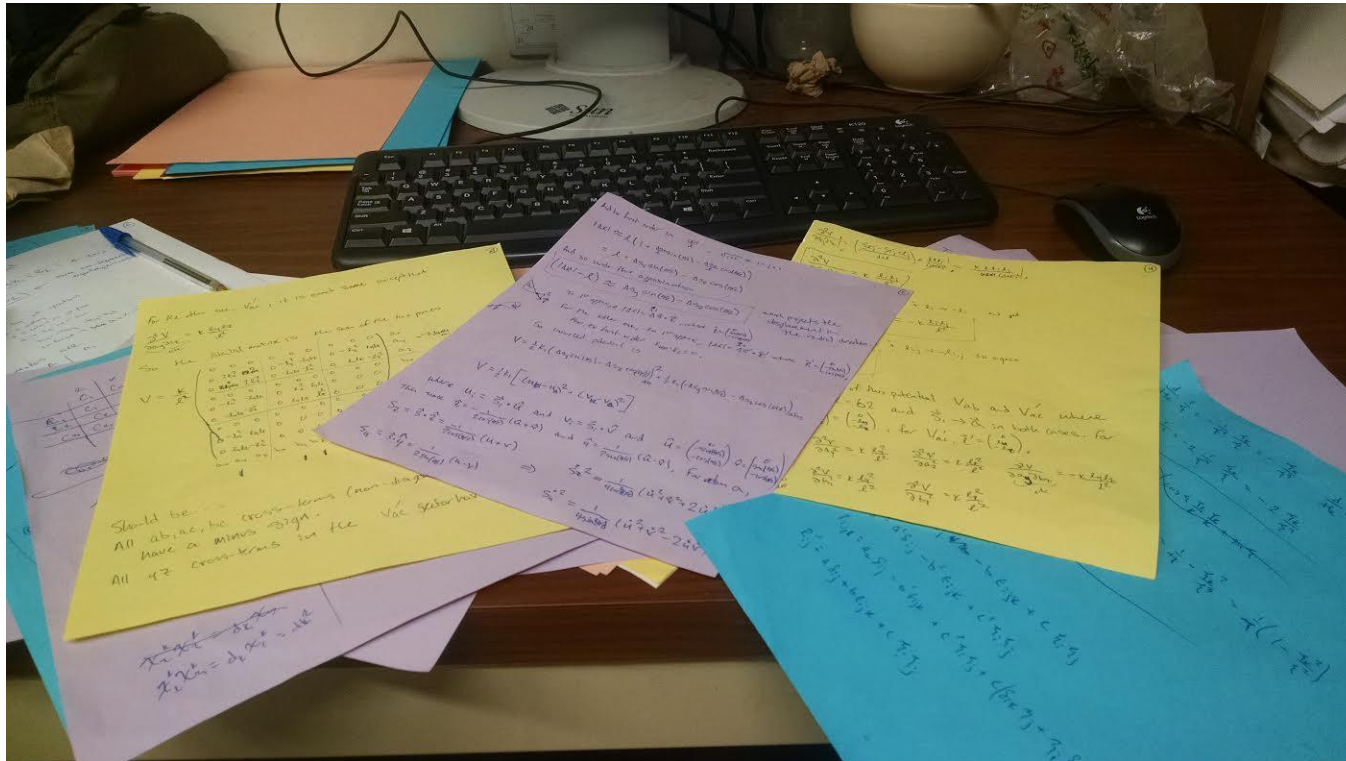
Simple matter of finding eigenvalues and eigenvectors

# Solving Vibrational Problems... So easy!!

...right?



- How to model the potential?
- 9x9 matrix.
- Don't screw up your partials!



Model needs Simplicity, Complexity, Symmetry, Accuracy.

**Forget it!** ----- What can SYMMETRY ALONE tell us?



J. SCHINDLER 2015

# GROUP THEORY *in*

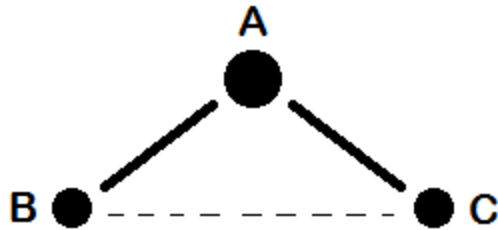
## Molecular Vibration

YOUR MIND IS THE SCENE OF THE CRIME.

WARNER BROS. PICTURES PRESENTS  
MARION COTILLARD ELLEN PAGE TONY HADRIY COLLEEN MURPHY TOM HEECHES and MICHAEL CAINE  
PRODUCED BY GUY HENRIOT & GUY  
DIRECTED BY GUY HENRIOT & GUY  
EXECUTIVE PRODUCERS CHRIS BRIGHAM THOMAS TULL PRODUCED BY EMMA THOMAS CHRISTOPHER NOLAN  
SCREENPLAY BY CHRISTOPHER NOLAN  
inceptionmovie.com  
EXPERIENCE IT JULY 16 IN THEATERS AND IMAX

# Deduce Vibrations of H<sub>2</sub>O with Group Theory

- 1) Find H<sub>2</sub>O symmetry group.
- 2) What rep acts on our coord space?
- 3) Find which irreps correspond to a normal mode.
- 4) Get degeneracies and eigenvectors.



Type I (Oxygen): A

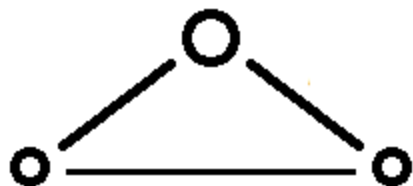
Type II (Hydrogen): B, C



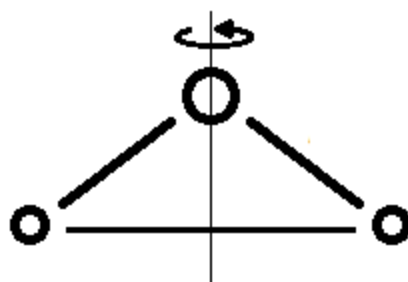
Symmetry Group of Water Molecule in 3D

$$C_{2v} = \{e, C_{2z}, \sigma_x, \sigma_y\}$$

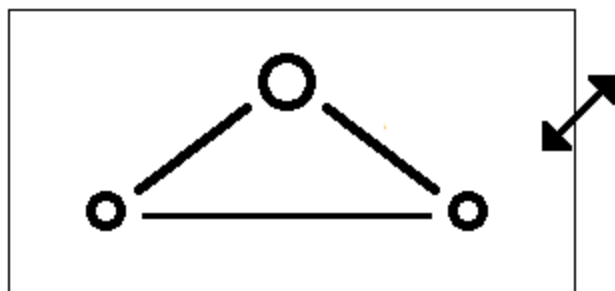
Identity:  $e$



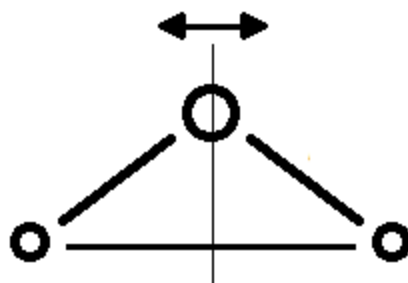
180° Rotation About z-Axis:  $C_{2z}$



Reflection Across x-Axis:  $\sigma_x$



Reflection Across y-Axis:  $\sigma_y$



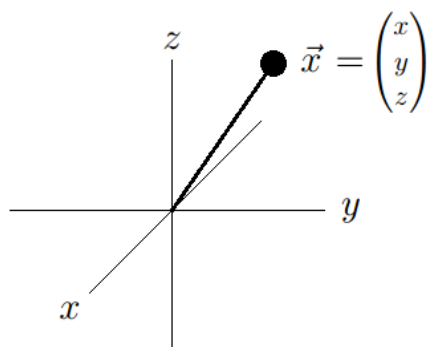
$C_{2v}$  Multiplication Table

e	r	x	y
r	e	y	x
x	y	e	r
y	x	r	e

$C_{2v}$  Character Table

$C_{2v}$	e	r	x	y
$A_1$	1	1	1	1
$A_2$	1	1	-1	-1
$B_1$	1	-1	1	-1
$B_2$	1	-1	-1	1

How does  $C_{2v}$  act on 3d space?



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

$$\text{Tr } R_e = 3$$

$$R_r = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\text{Tr } R_r = -1$$

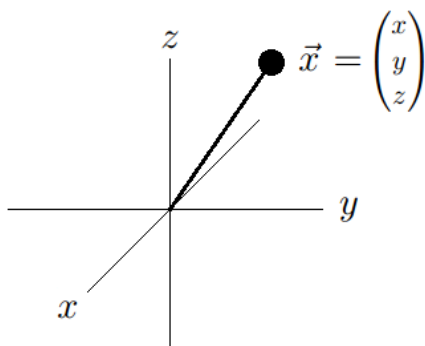
$$R_x = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\text{Tr } R_x = 1$$

$$R_y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\text{Tr } R_y = 1$$

How does  $C_{2v}$  act on 3d space?



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

$$\text{Tr } R_e = 3$$

$$R_r = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\text{Tr } R_r = -1$$

$$R_x = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\text{Tr } R_x = 1$$

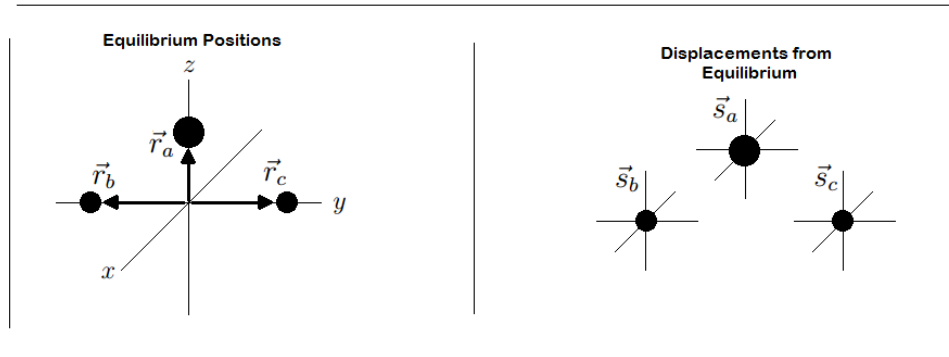
$$R_y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\text{Tr } R_y = 1$$

For example

$$R_r \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

Define coordinate system for problem:



position  
vector

fixed  
equilibrium point

displacement  
from eq.

$$\vec{x}_i = \vec{r}_i + \vec{s}_i$$

The diagram is divided into two parts by a vertical line. The left part, titled "Equilibrium Positions", shows a 3D coordinate system with axes  $x$ ,  $y$ , and  $z$ . Three particles are located at equilibrium positions: particle  $a$  is on the  $z$ -axis, particle  $b$  is on the  $x$ -axis, and particle  $c$  is on the  $y$ -axis. Vectors  $\vec{r}_a$ ,  $\vec{r}_b$ , and  $\vec{r}_c$  point from the origin to each particle. The right part, titled "Displacements from Equilibrium", shows the same three particles displaced from their equilibrium positions. Vectors  $\vec{s}_a$ ,  $\vec{s}_b$ , and  $\vec{s}_c$  represent the displacements from the origin to the new positions of particles  $a$ ,  $b$ , and  $c$  respectively.

position vector      fixed equilibrium point      displacement from eq.

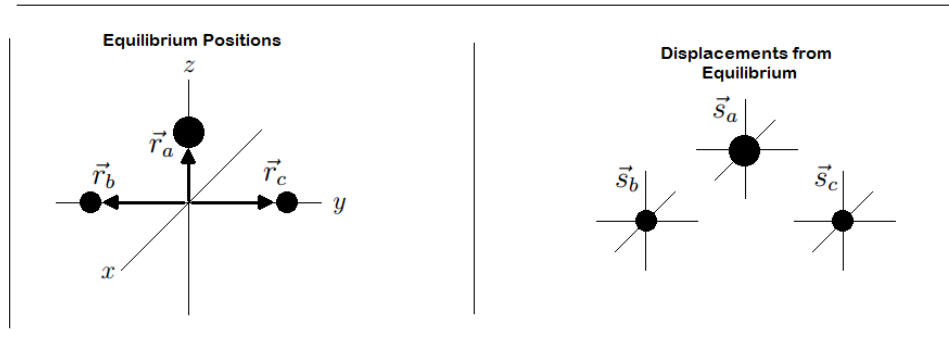
$\vec{x}_i = \vec{r}_i + \vec{s}_i$

$$R_g \vec{r}_i = \vec{r}_j \quad \text{where} \quad \begin{array}{l} g \in G \\ i, j = \text{same type} \end{array}$$

$$R_g \vec{r}_i = \vec{r}_j \quad \text{where} \quad \begin{array}{l} g \in G \\ i, j = \text{same type} \end{array}$$



Define coordinate system for problem:



$$\begin{array}{ccccc} \text{position} & & \text{fixed} & & \text{displacement} \\ \text{vector} & & \text{equilibrium point} & & \text{from eq.} \\ & \swarrow & | & \searrow & \\ & \vec{x}_i = \vec{r}_i + \vec{s}_i & & & \end{array}$$

Symmetry operations, by definition:

$$R_g \vec{r}_i = \vec{r}_j \quad \text{where} \quad \begin{array}{l} g \in G \\ i, j = \text{same type} \end{array}$$

Therefore:

**IMPORTANT**

$$\begin{aligned} R\vec{x}_i &= R\vec{r}_i + R\vec{s}_i \\ &= \vec{r}_j + R\vec{s}_i \end{aligned} \quad \Rightarrow \quad \vec{s}_j' = R\vec{s}_i$$

Which is an equivalent physical configuration!

Figure 1 consists of two diagrams. The left diagram, titled "Equilibrium Positions", shows three particles (black dots) in a 3D coordinate system with axes  $x$ ,  $y$ , and  $z$ . Particle  $a$  is on the  $z$ -axis, particle  $b$  is on the  $x$ -axis, and particle  $c$  is on the  $y$ -axis. Vectors  $\vec{r}_a$ ,  $\vec{r}_b$ , and  $\vec{r}_c$  point from the origin to each particle. The right diagram, titled "Displacements from Equilibrium", shows the same three particles with displacement vectors  $\vec{s}_a$ ,  $\vec{s}_b$ , and  $\vec{s}_c$  originating from their equilibrium positions. Each displacement vector is perpendicular to its corresponding equilibrium position vector.

position vector      fixed equilibrium point      displacement from eq.

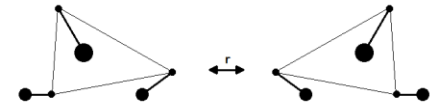
$\vec{x}_i = \vec{r}_i + \vec{s}_i$

$$R_g \vec{r}_i = \vec{r}_j \quad \text{where} \quad \begin{array}{l} g \in G \\ i, j = \text{same type} \end{array}$$

**IMPORTANT**

$$\begin{aligned} R\vec{x}_i &= R\vec{r}_i + R\vec{s}_i \\ &= \vec{r}_j + R\vec{s}_i \end{aligned} \quad \implies \quad \vec{s}_j' = R\vec{s}_i$$

**Can't change the frequency!**



**Which is an equivalent physical configuration!**

# Aside: Notation

Notation

$$\vec{a} \equiv \vec{s}_a = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}$$

$$\vec{b} \equiv \vec{s}_b = \begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix}$$

$$\vec{c} \equiv \vec{s}_c = \begin{pmatrix} c_x \\ c_y \\ c_z \end{pmatrix}$$

Coordinate Vector

$$\vec{q} = \begin{pmatrix} a_x \\ a_y \\ a_z \\ b_x \\ b_y \\ b_z \\ c_x \\ c_y \\ c_z \end{pmatrix}$$

Normal modes

$$\vec{\xi}^{(i)} = \begin{pmatrix} \xi_{ax} \\ \xi_{ay} \\ \xi_{az} \\ \xi_{bx} \\ \xi_{by} \\ \xi_{bz} \\ \xi_{cx} \\ \xi_{cy} \\ \xi_{cz} \end{pmatrix}$$

# Aside: Notation

Normal modes form an orthogonal basis  
(by eigen thm of linear algebra)

$$\vec{q} = \sum_i c_i \vec{\xi}^{(i)}$$

---

In standard basis

$$\vec{q} = \begin{pmatrix} a_x \\ a_y \\ a_z \\ b_x \\ b_y \\ b_z \\ c_x \\ c_y \\ c_z \end{pmatrix}$$

$\longleftrightarrow$   
**S**  
change of basis  
matrix  
 $\longleftrightarrow$

Normal Coordinates

$$\vec{q} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \\ c_7 \\ c_8 \\ c_9 \end{pmatrix}$$

OK, back to it...

How does  $C_{2v}$  act on coordinate space?

- Rep on coordinate space is equivalent to rep in normal mode space.
- Each frequency eigenspace is an invariant subspace of the representation!!
- Thus each frequency eigenspace corresponds to some irrep of G such that:

$$\begin{array}{ccc} \text{dimension of} & & \text{dimension of} \\ \text{frequency eigenspace} & = & \text{corresponding irrep} \end{array}$$

eigenvector symmetry  
reflects the corresponding irrep

- Use characters to deduce which irreps are present. Then eliminate translations and rotations and identify eigenvectors using symmetry.

How does  $C_{2v}$  act on coordinate space?

May or may not switch the Hydrogens. Acts R on each block.

$$r \cdot q \longrightarrow \Delta(R_r)q = \left[ \begin{array}{c|c|c} R_r & 0 & 0 \\ \hline 0 & 0 & R_r \\ \hline 0 & R_r & 0 \end{array} \right] \begin{bmatrix} \vec{a} \\ \vec{b} \\ \vec{c} \end{bmatrix}$$

$$= \left[ \begin{array}{ccc|ccc|ccc} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ \hline 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{array} \right] \begin{bmatrix} a_x \\ a_y \\ a_z \\ b_x \\ b_y \\ b_z \\ c_x \\ c_y \\ c_z \end{bmatrix}$$



$\Delta(R)$  is the reducible rep of  $C_{2v}$  on the coordinate space.

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

$$R_r = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$R_x = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$R_y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\Delta(R_e) = \left[ \begin{array}{c|c|c} R & 0 & 0 \\ \hline 0 & R & 0 \\ \hline 0 & 0 & R \end{array} \right]$$

$$\Delta(R_r) = \left[ \begin{array}{c|c|c} R & 0 & 0 \\ \hline 0 & 0 & R \\ \hline 0 & R & 0 \end{array} \right]$$

$$\Delta(R_x) = \left[ \begin{array}{c|c|c} R & 0 & 0 \\ \hline 0 & R & 0 \\ \hline 0 & 0 & R \end{array} \right]$$

$$\Delta(R_y) = \left[ \begin{array}{c|c|c} R & 0 & 0 \\ \hline 0 & 0 & R \\ \hline 0 & R & 0 \end{array} \right]$$

$$\chi(e) = 9$$

$$\chi(r) = -1$$

$$\chi(x) = 3$$

$$\chi(y) = 1$$

### $C_{2v}$ Character Table

$C_{2v}$	e	r	x	y
$A_1$	1	1	1	1
$A_2$	1	1	-1	-1
$B_1$	1	-1	1	-1
$B_2$	1	-1	-1	1

$$n_i = \frac{1}{N_G} \sum_g \chi(g)^* \chi_i(g)$$

Composition of  $\Delta$  in terms of irreps:

$$\Delta = 3A_1 + A_2 + 3B_1 + 2B_2$$

3 internal vibrations

+ 3 translations

+ 3 rotations

---

= 9 d.o.f. = 9 irreps = 9 modes

# How many reps?

## Translations

	$e =$ $r =$ $x =$ $y =$	?
--	----------------------------------	---

	$e =$ $r =$ $x =$ $y =$	?
--	----------------------------------	---

	$e =$ $r =$ $x =$ $y =$	?
--	----------------------------------	---

$$\begin{aligned} \text{Total} &= 3A1 + A2 + 3B1 + 2B2 \\ \text{Translations} &= A1 + B1 + B2 \\ \text{+ Rotations} &= A2 + B1 + B2 \\ &= A1 + A2 + 2B1 + 2B2 \end{aligned}$$

$$\text{Internal} = 2A1 + B1$$

## Rotations

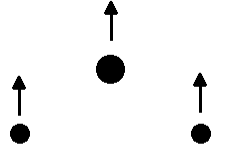

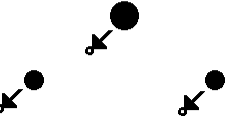
	$e =$ $r =$ $x =$ $y =$	?
--	----------------------------------	---

	$e =$ $r =$ $x =$ $y =$	?
--	----------------------------------	---

	$e =$ $r =$ $x =$ $y =$	?
--	----------------------------------	---

# How many reps?

## Translations


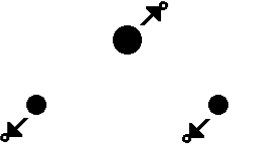
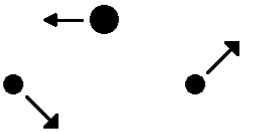
	$e = 1$ $r = 1$ $x = 1$ $y = 1$	<b>A1</b>
	$e = 1$ $r = -1$ $x = 1$ $y = -1$	<b>B1</b>
 (out of page)	$e = 1$ $r = -1$ $x = -1$ $y = 1$	<b>B2</b>

$$\text{Total} = 3A1 + A2 + 3B1 + 2B2$$

$$\begin{aligned} \text{Translations} &= A1 + B1 + B2 \\ \text{+ Rotations} &= A2 + B1 + B2 \\ &= A1 + A2 + 2B1 + 2B2 \end{aligned}$$

$$\text{Internal} = 2A1 + B1$$

## Rotations

	$e = 1$ $r = 1$ $x = -1$ $y = -1$	<b>A2</b>
	$e = 1$ $r = -1$ $x = -1$ $y = 1$	<b>B2</b>
	$e = 1$ $r = -1$ $x = 1$ $y = -1$	<b>B1</b>

# Internal Vibrations: B1 Mode

<b>B1</b>	$e = 1$ $r = -1$ $x = 1$ $y = -1$	<b>?</b>
-----------	--	----------



## The math way:

$$-\sigma_y \begin{pmatrix} a_x \\ a_y \\ a_z \\ b_x \\ b_y \\ b_z \\ c_x \\ c_y \\ c_z \end{pmatrix} = \begin{pmatrix} -a_x \\ a_y \\ -a_z \\ -c_x \\ c_y \\ -c_z \\ -b_x \\ b_y \\ -b_z \end{pmatrix} = \begin{pmatrix} a_x \\ a_y \\ a_z \\ b_x \\ b_y \\ b_z \\ c_x \\ c_y \\ c_z \end{pmatrix}$$

$$\underline{x=1} \Rightarrow$$

$$ax=bx=cx=0$$

$$\underline{y=-1} \Rightarrow$$

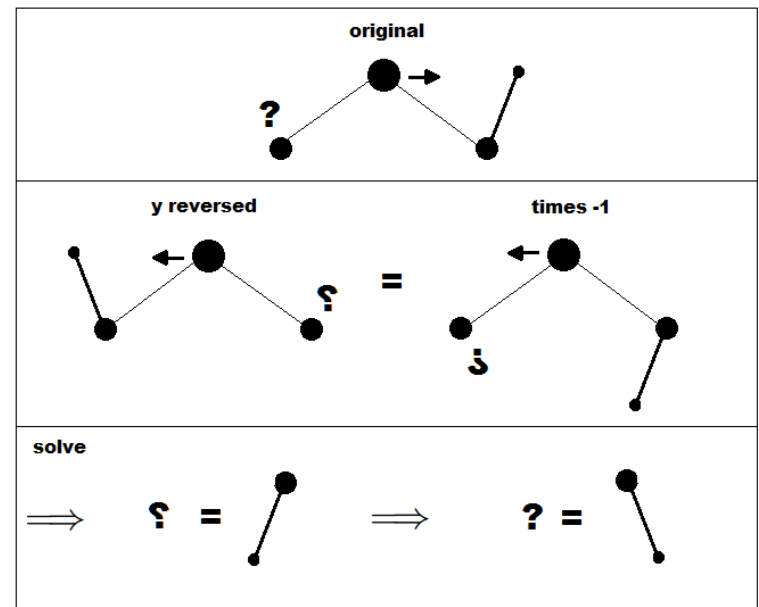
$$az=0$$

$$cy=by$$

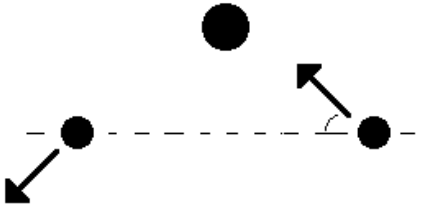
$$cz=-bz$$

or

## A strange equation:

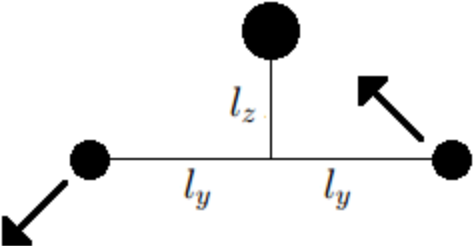


## Internal Vibrations: B1 Mode

<b>B1</b>	$\begin{aligned}e &= 1 \\r &= -1 \\x &= 1 \\y &= -1\end{aligned}$	 <p><math>xx=0 \quad a=ay \quad cy=by \quad cz=-bz</math></p>
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## B1 Mode

**Can write specific eigenvector by choosing a frame. For example, the frame where  $a=0$  and  $L=0$  (oxygen at origin and zero angular momentum).**

<b>B1</b>	$\begin{aligned} \mathbf{e} &= 1 \\ \mathbf{r} &= -1 \\ \mathbf{x} &= 1 \\ \mathbf{y} &= -1 \end{aligned}$	<p>frame where <math>a=0</math> <math>L=0</math></p>  <p>(eigenvectors parallel to arms)</p>
$\vec{a} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \quad \vec{b} = \begin{pmatrix} 0 \\ -l_y \\ -l_z \end{pmatrix} \quad \vec{c} = \begin{pmatrix} 0 \\ -l_y \\ l_z \end{pmatrix}$		



**And so on for the rest of the modes...**

**In some cases the eigenvectors are completely determined by symmetry, in other cases they are constrained but not entirely determined. For example, the form of water's two A<sub>1</sub> modes is constrained but not determined by the procedure we've used here.**



**Thanks!**