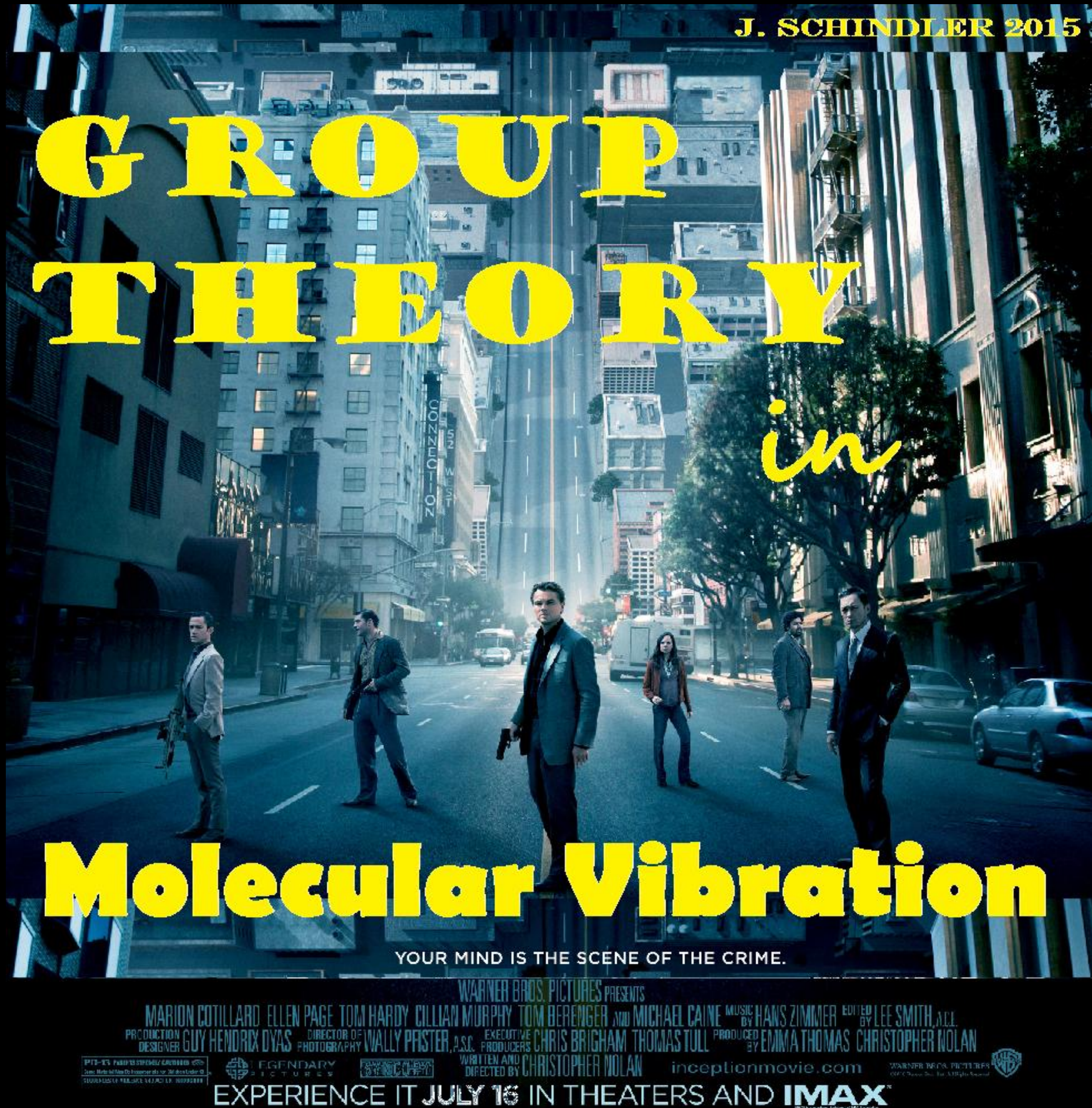
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in
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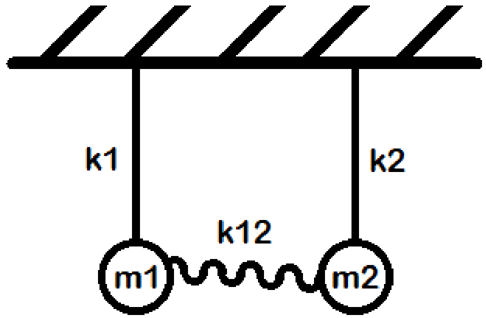
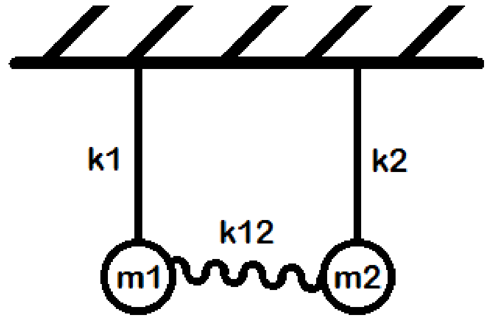
Solving Vibrational Problems…   So easy!!



Normal Modes

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

Solving Vibrational Problems… So easy!!



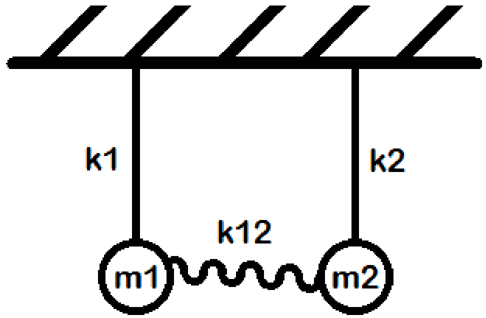
Normal Modes

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

eigenvectors

frequencies

Solving Vibrational Problems… So easy!!



Normal Modes

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

Quadratic Lagrangian

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

Linearized Potential

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

about a (quasi-)stable equilibrium

Equations of Motion

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

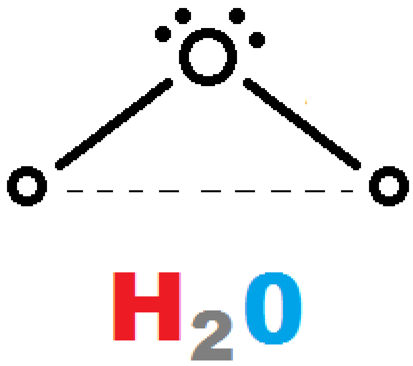
Equations of Motion

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

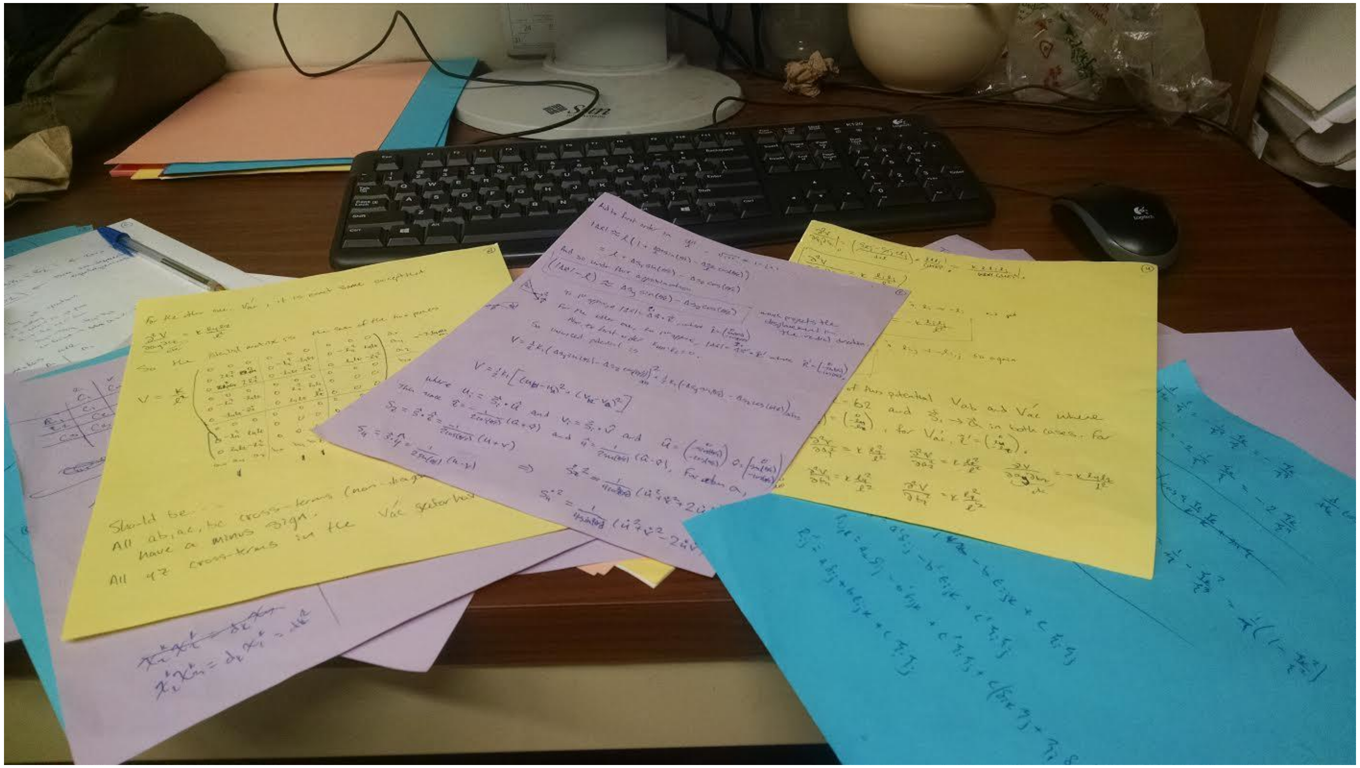
Simple matter of finding eigenvalues and eigenvectors

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?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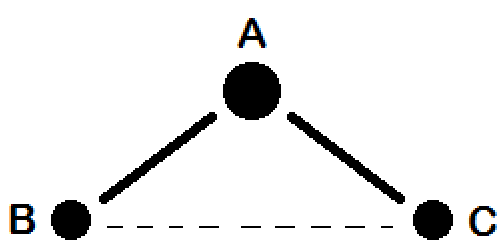
Deduce Vibrations of H_20 with Group Theory

1) Find H_20 symmetry group.
2) What rep acts on our coord space?
3) Find which irreps correspond to a normal mode.
4) Get degeneracies and eigenvectors.



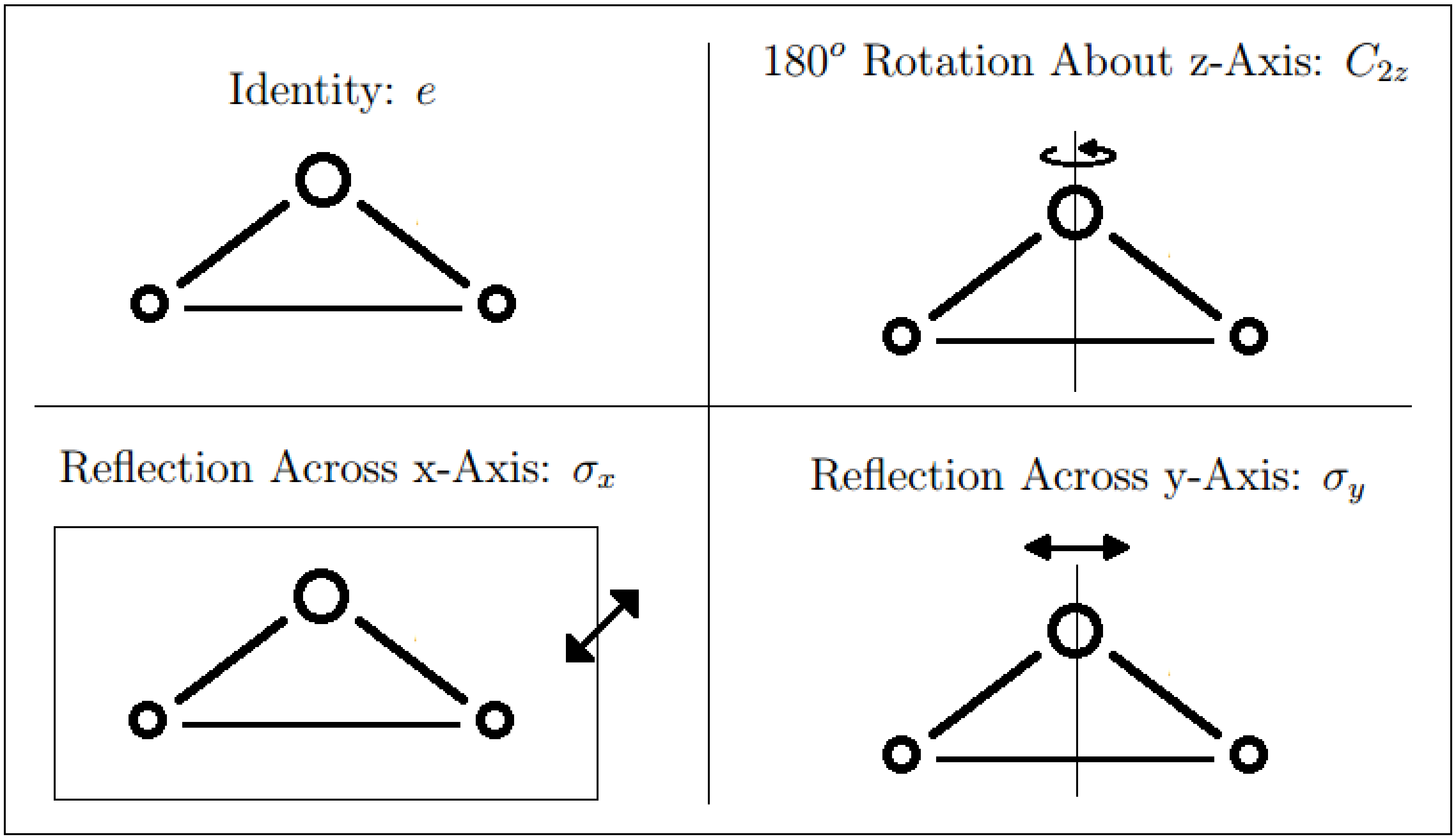
Type I (Oxygen): A

Type II (Hydrogen): B, C

Symmetry transformation of equilibrium state permutes atoms of the same type.

Symmetry Group of Water Molecule in 3D

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



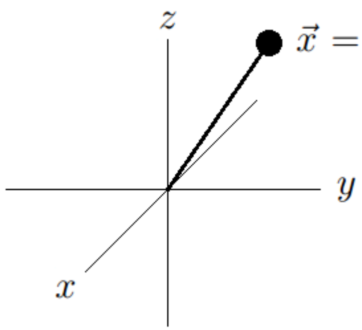
C_{2v} **Multiplication Table**

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?



$$\vec{x} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

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

$\mathrm{Tr}\, R_e = 3$

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

$\mathrm{Tr}\, R_r = -1$

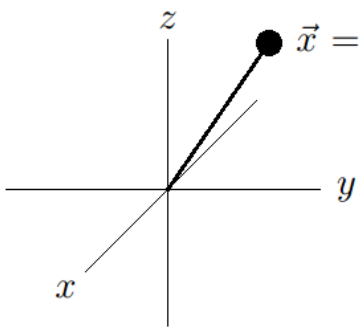
$$R_x = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$\mathrm{Tr}\, R_x = 1$

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

$\mathrm{Tr}\, R_y = 1$

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



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$\mathrm{Tr}\, R_r = -1$

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

$\mathrm{Tr}\, R_x = 1$

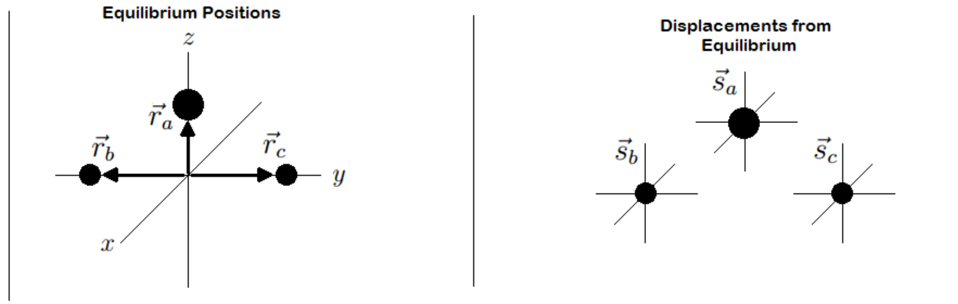
$$R_y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$\mathrm{Tr}\, R_y = 1$

For example

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

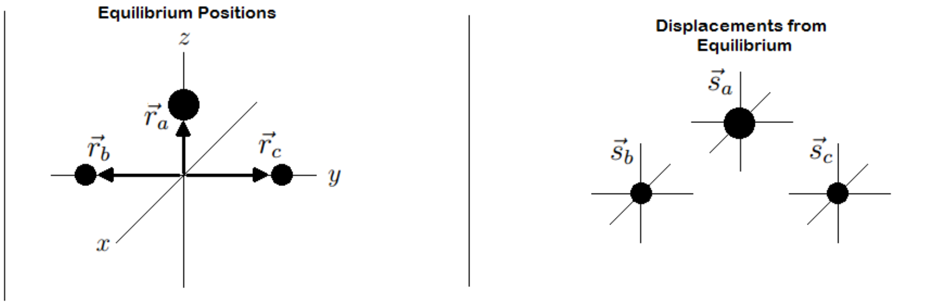
Define coordinate system for problem:



position vector — **fixed equilibrium point** — **displacement from eq.**

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

Define coordinate system for problem:



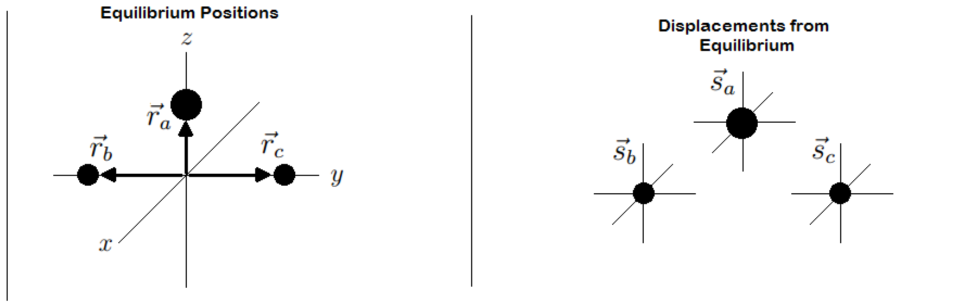
position vector — fixed equilibrium point — displacement from eq.

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

Symmetry operations, by definition:

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

Define coordinate system for problem:



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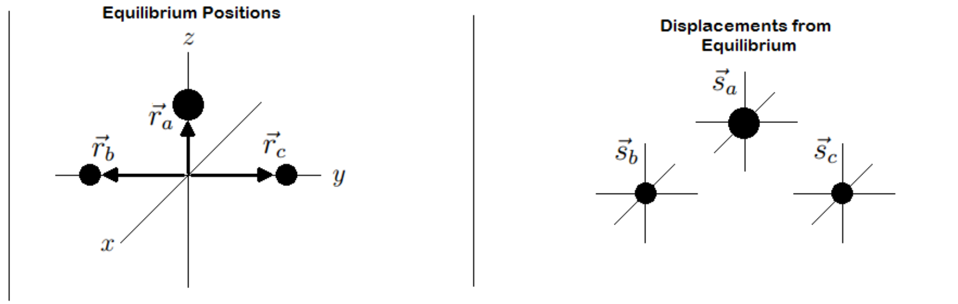
Therefore:

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

Which is an <u>equivalent physical configuration</u>!

Define coordinate system for problem:



position vector — fixed equilibrium point — displacement from eq.

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

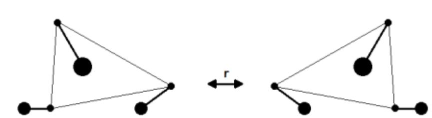
Symmetry operations, by definition:

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

Therefore:

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

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

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

S ⟷ change of basis matrix

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:

dimension of frequency eigenspace = dimension of corresponding irrep

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.

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

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

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

$$R_e = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad R_r = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad R_x = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad R_y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

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

$$\chi(e) = 9 \quad \chi(r) = -1 \quad \chi(x) = 3 \quad \chi(y) = 1$$

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 Δ in terms of irreps:

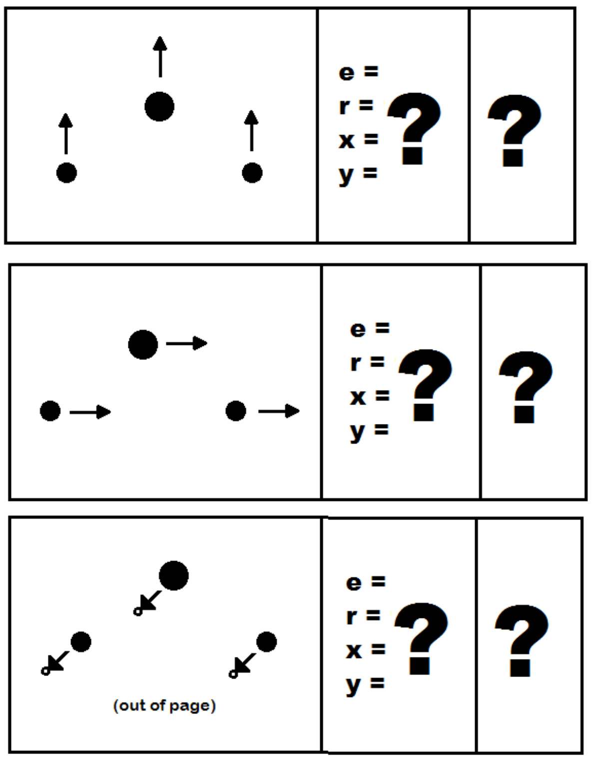
$$\Delta = 3A_1 + A_2 + 3B_1 + 2B_2$$

3 internal vibrations
+ 3 translations
+ 3 rotations

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

How many reps?

Translations

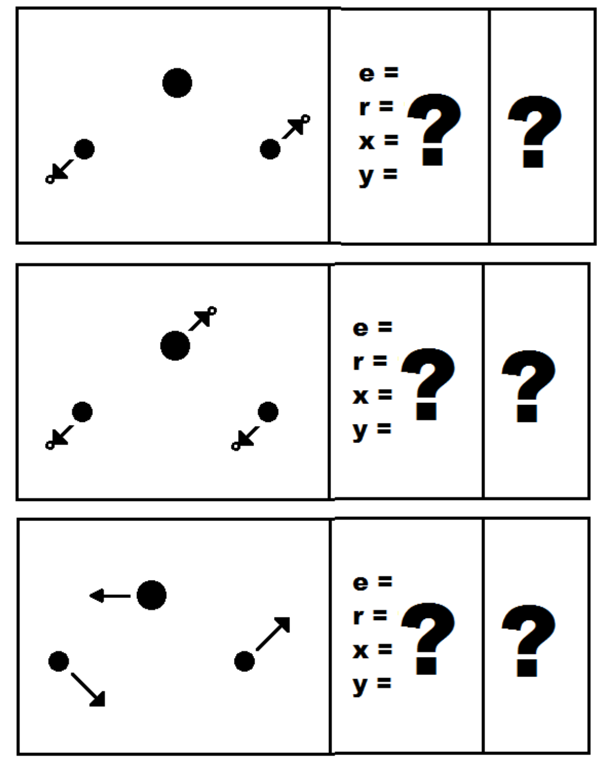


Total = 3A1+A2+3B1+2B2

Translations =	A1		+B1	+B2
+ Rotations =		A2	+B1	+B2
=	A1	+A2	+2B1	+2B2

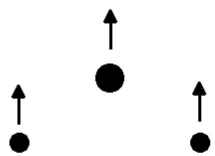
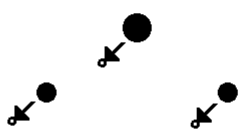
Internal = 2A1 +B1

Rotations

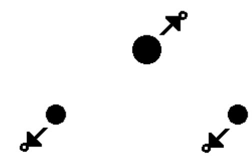
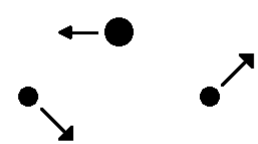


How many reps?

Translations

	e = 1 r = 1 x = 1 y = 1	A1
	e = 1 r = -1 x = 1 y = -1	B1
 (out of page)	e = 1 r = -1 x = -1 y = 1	B2

Rotations

	e = 1 r = 1 x = -1 y = -1	A2
	e = 1 r = -1 x = -1 y = 1	B2
	e = 1 r = -1 x = 1 y = -1	B1

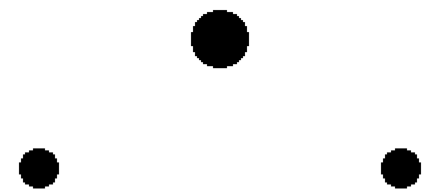
Total = 3A1+A2+3B1+2B2

Translations = A1 +B1 +B2
+ Rotations = A2 +B1 +B2
= A1+A2+2B1+2B2

Internal = 2A1 +B1

Internal Vibrations: B1 Mode

B1	e = 1 r = -1 x = 1 y = -1	?



The math way:

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

x=1 $\Longrightarrow$

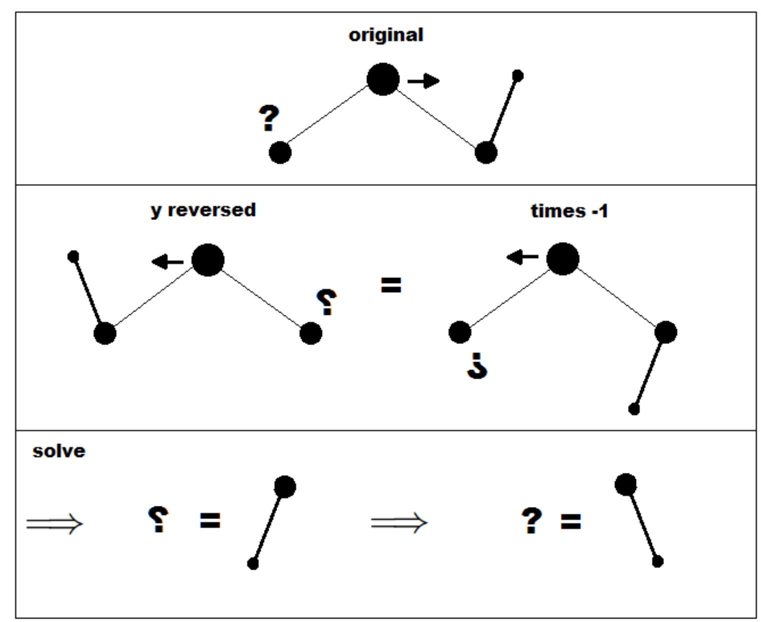
ax=bx=cx=0

y=-1 $\Longrightarrow$

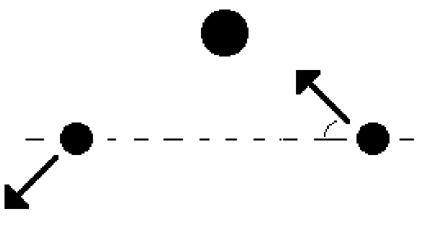
az=0
cy=by
cz=-bz

or

A strange equation:

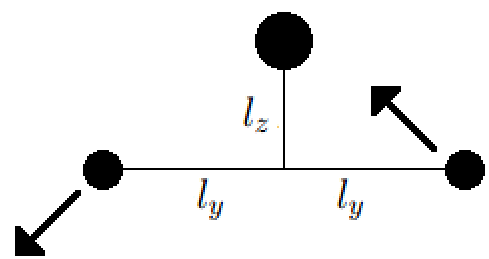


Internal Vibrations: B1 Mode

B1	e = 1 r = -1 x = 1 y = -1	 xx=0 a=ay cy=by cz=-bz

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).

<table>
<tr>
<td>B1</td>
<td>e = 1
r = -1
x = 1
y = -1</td>
<td>frame where a=0 L=0

(eigenvectors parallel to arms)</td>
</tr>
<tr>
<td colspan="3">$\vec{a} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$ $\vec{b} = \begin{pmatrix} 0 \\ -l_y \\ -l_z \end{pmatrix}$ $\vec{c} = \begin{pmatrix} 0 \\ -l_y \\ l_z \end{pmatrix}$</td>
</tr>
</table>

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 A1 modes is constrained but not determined by the procedure we've used here.

Thanks!