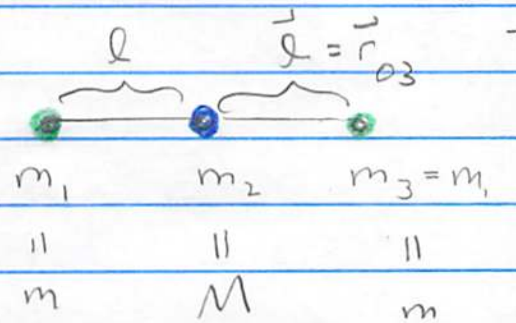
Vibrations of Molecules

- For example,



Take a linear molecule in 3D. The masses are m_a, the coordinates are:

$$\boxed{\vec{r}_a = \vec{r}_{0a} + \delta\vec{r}_a}$$

- This is a 9-dimensional space: $X = (\delta\vec{r}_1, \delta\vec{r}_2, \delta\vec{r}_3)$

  $3 \cdot 3 = 9$ variables and normal modes

- But there are three translational zero modes

Translation in x, y, z (x shown)

$\vec{E}_0 \propto (\hat{x}, \hat{x}, \hat{x})$

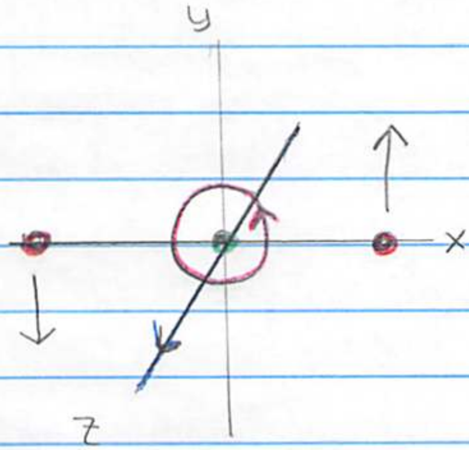
→ The remaining non-zero modes should be orthogonal to $\vec{E}_0$. As in the previous example this is equivalent to requiring that the non-zero modes should have no net momentum

$$\sum_a m_a \delta\dot{\vec{r}}_a = 0 \quad \text{or} \quad \boxed{\sum_a m_a \delta\vec{r}_a = 0}$$

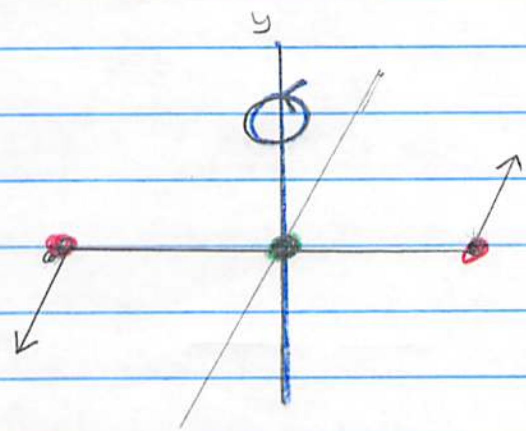
the center of mass is not displaced for non-zero eigenmodes

- See proof at end for angular momentum case and previous example.

- There are <u>two</u> rotational zero modes



- Rotation around z



- Rotation around y

- Normally, there would be a third zero mode corresponding to rotations about the x-axis. But here, since the molecule is linear, rotations around the x-axis do not displace the atoms and there is no zero-mode associated with the x-rotation

The total # of non-zero modes is

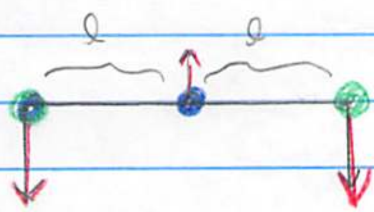
$$9 - 5 = 4$$

- The non-zero modes should be orthogonal to the rotational zero modes. Similarly to the momentum conservation case this is equivalent to the statement that non-zero modes should have no angular momentum

$$\boxed{\sum_a m_a (\vec{r}_{0a} \times \delta \vec{r}_a) = 0}$$

You should convince yourself of this. See proof at end.

- Now lets consider the bending in the y-direction



- There are three y-coords $y_1, y_2\ y_3$
- But the y-momentum and the angular momentum in the z-direction (out of the page) should be zero so

$$m y_1 + M y_2 + m y_3 = 0 \qquad (\text{No } P^y)$$

and

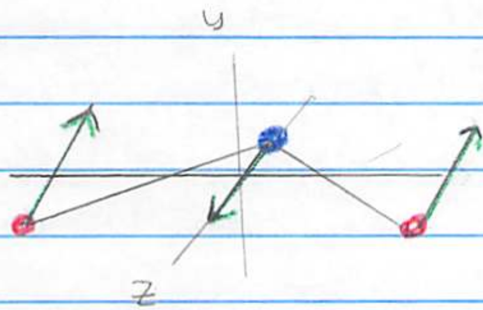
$$l m y_1 - l m y_3 = 0 \qquad (\text{No } L^z)$$

So the third mode must have

a "bending" mode

$$(y_1, y_2, y_3) \propto (1, -2m/M, 1)$$

- Finally there is another bending mode (with the same frequency as the y-bend) in the z-direction

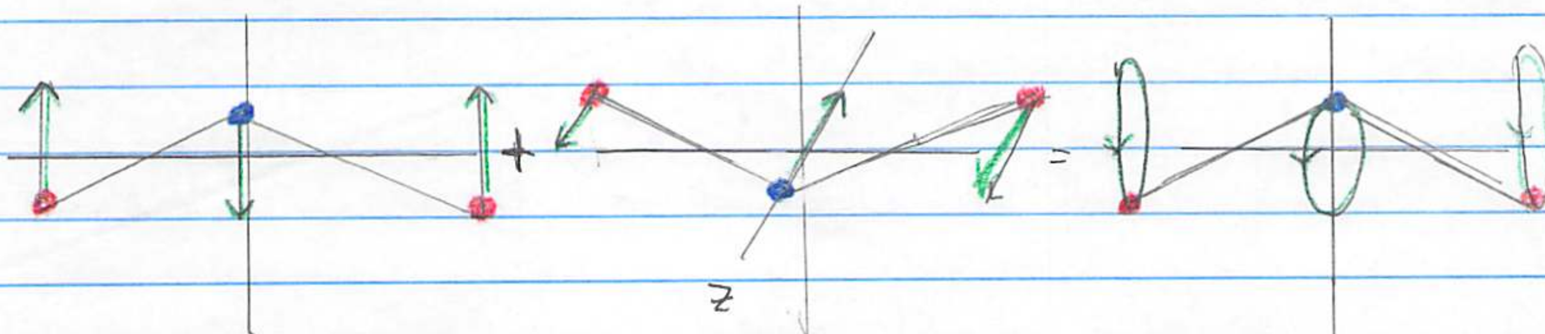


<u>Summary</u>

9 modes = 3-trans zero + 2-rot zero

+ 2 vibration in x + 2 bendings in y and z

- Finally, the two bending modes have the same frequency and can be combinded into a whirling mode:

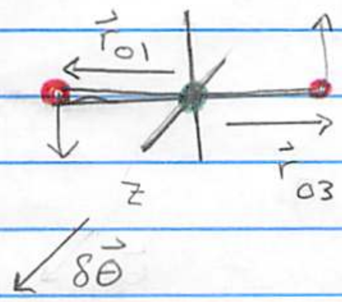


See video! (click me!)

This is a proof of the statement on page 3 that requiring that non-zero modes are orthogonal to the rotational zero modes means that the non-zero modes will have no net angular momentum. A similar statement was mage on page 1 regarding the momentum.

Proof

- Consider a rotation around z:



$$\vec{E}_\theta = (\delta\vec{\theta} \times \vec{r}_{01}, \delta\vec{\theta} \times \vec{r}_{02}, \delta\vec{\theta} \times \vec{r}_{03})$$

↑ this is a zero mode: a rotation by $\delta\vec{\theta}$

- Then for a generic displacement:

$$\vec{Y} = (\delta\vec{r}_1, \delta\vec{r}_2, \delta\vec{r}_3)$$

Requiring orthogonality means $\quad$ use $\vec{a}\cdot\vec{b}\times\vec{c} = \vec{b}\cdot\vec{c}\times\vec{a}$

$$(E_\theta, \mathbb{M}\vec{Y}) = \sum_a m_a (\delta\vec{\theta} \times \vec{r}_{0a}) \cdot \delta\vec{r} = 0$$

$$= \sum_a m_a (\vec{r}_{0a} \times \delta\vec{r}_a) \cdot \delta\vec{\theta} = 0$$

Or since $\delta\vec{\theta}$ is arbitrary:

$$\boxed{\sum_a m_a (\vec{r}_{0a} \times \delta\vec{r}_a) = 0}$$

So, The angular momentum carried by the non-zero modes is zero: