The Orthogonality Theorem and No Mixing

- We have noted that by change of basis we may block diagonize the group matrices

$$O \to \underline{O}_{ab} = S^{-1} O S$$

$$= D^{(1)} \oplus D^{(2)} \oplus 2D^{(3)}$$

- This means that we may shift from our canonical basis to another basis, Where each of the elements of the new basis transform according to an irrep of the group. The advantage is that H (the hamiltonian or potential energy matrix) will be block diagonalized in this basis due to the following theorem:

Thrm
- let H be a operator / matrix wich commutes with the group operator O_g.
- Let $\langle \, , \rangle$ denote a group invariant inner product. By this we mean for

$$\langle \vec{x}, \vec{y} \rangle = \langle O_g \vec{x}, O_g \vec{y} \rangle = \langle \vec{x}, O_g^{\dagger} O_g \vec{y} \rangle$$

So $O^{\dagger}_g O_g$ =1 should be unitary

So a group invariant $\langle , \rangle$ implies O_g are unitary $O_g^{\dagger} O_g = 1$

- Let $\vec{\phi}_a^{(\mu)}$ and $\vec{f}_b^{(\nu)}$ be two vectors transforming as a representation of G i.e.

$$O_g \vec{\Phi}_a^{(\mu)} = \vec{\Phi}_c^{(\mu)} D_{ca}^{(\mu)}(g) \qquad (\star)$$

$$O_g \vec{f}_b^{(\nu)} = \vec{f}_d^{(\nu)} D_{bd}^{(\nu)}(g) \qquad (\star\star)$$

"typo" should read $O_g\vec{f}_b^{(\nu)} = \vec{f}_d^{(\nu)} D_{db}^{(\nu)}(g)$

- We say that $\vec{\phi}_a^{(\mu)}$ "belongs to the a-th row of the irreducable representation μ"

- Then the matrix elements

$$\boxed{\langle \vec{\Phi}_a^{(\mu)}, H \vec{f}_b^{(\nu)} \rangle = h^{(\mu)} \delta_{ab} \delta_{\mu\nu}}$$

are diagonal in a, b and μ, ν and $h^{(\mu)}$ is independent of a (the row of the rep)

$$h_\mu = \frac{1}{n_\mu} \sum_c \langle \vec{\phi}_c^{(\mu)}, H \vec{f}_c^{(\nu)} \rangle$$

Proof

$$\langle \vec{\Phi}_a^{(\mu)}, H \vec{f}_b^{(\nu)} \rangle = \frac{1}{n_G} \sum_g \langle O_g \vec{\Phi}_a^{(\mu)}, O_g H \vec{f}_b^{(\nu)} \rangle$$

- So using the transformation rules $(\star)$ and $(\star\star)$ and the fact that $O_g H = H O_g$ yields

$$\langle \phi_a^{(\mu)}, H \vec{f}_b^{(\nu)} \rangle = \frac{1}{n_G} \sum_g \langle \vec{\phi}_c^{(\mu)}, H \vec{f}_d^{(\nu)} \rangle \left(D_{ca}^{(\mu)}(g)\right)^* \left(D_{db}^{(\nu)}(g)\right)$$

Which by the orthogonality theorem yields

$$\langle \vec{\phi}_a^{(\mu)}, H \phi_b^{(\nu)} \rangle = \langle \vec{\phi}_c^{(\mu)}, H \vec{f}_d^{(\nu)} \rangle \frac{1}{n_\mu} \delta_{\mu\nu} \delta_{cd} \delta_{ab}$$

$$= h^{(\mu)} \delta_{\mu\nu} \delta_{ab}$$

So summing c the theorem follows.

- The full vector space decomposes as

$$O_g = D^{(1)} \oplus D^{(2)} \oplus 2D^{(3)} \qquad (\star)$$

So the "Hamiltonian" will take the form

$$\langle \vec{\phi}, H \vec{\phi} \rangle \sim \begin{pmatrix} \boxed{1\times1} & & & \\ & \boxed{1\times1} & & \\ & & \boxed{2\times2} & \\ & & & \boxed{2\times2} \end{pmatrix}$$

The $\boxed{2\times2}$ and $\boxed{2\times2}$ blocks for row 1 and row 2, are the same matrix since $h^{(\mu)}$ is independent of the row in thrm.

In a basis $\{ \{\vec{\phi}_1^{(1)}\}, \{\vec{\phi}_1^{(2)}\}, \{\vec{\phi}_{1,1}^{(3)}, \vec{\phi}_{1,2}^{(3)}\}$,
$\{\vec{\phi}_{2,1}^{(3)}, \vec{\phi}_{2,2}^{(3)}\} \}$

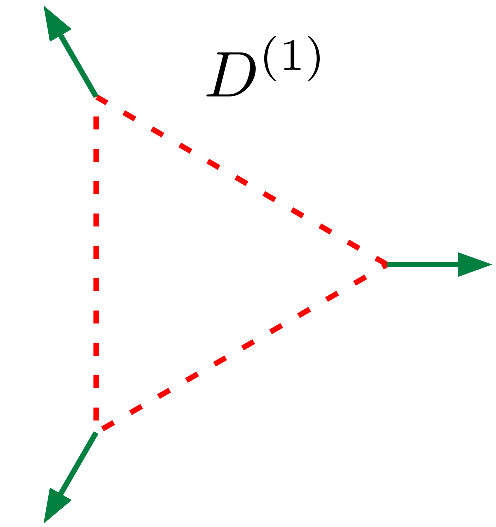
where

$\vec{\phi}_{a,i}^{(\mu)}$ is basis transforming in the a-th row of the μ-th rep; and i is a discrete index because there are in general more than one such functions. In this example there are two such functions because $D^{(3)}$ appears twice in Eq $\star$

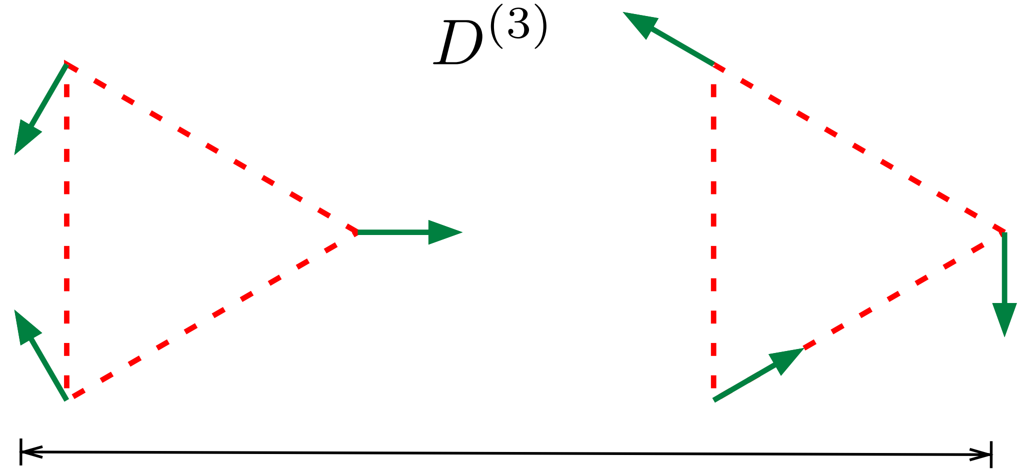
Vibrational Modes

This is a quick preview of the final answer. The six modes on the previous page will look like this. We also show to which repsentation, D, they belong.

$D^{(1)}$

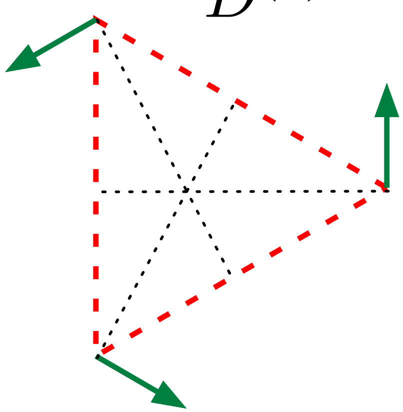


$D^{(3)}$

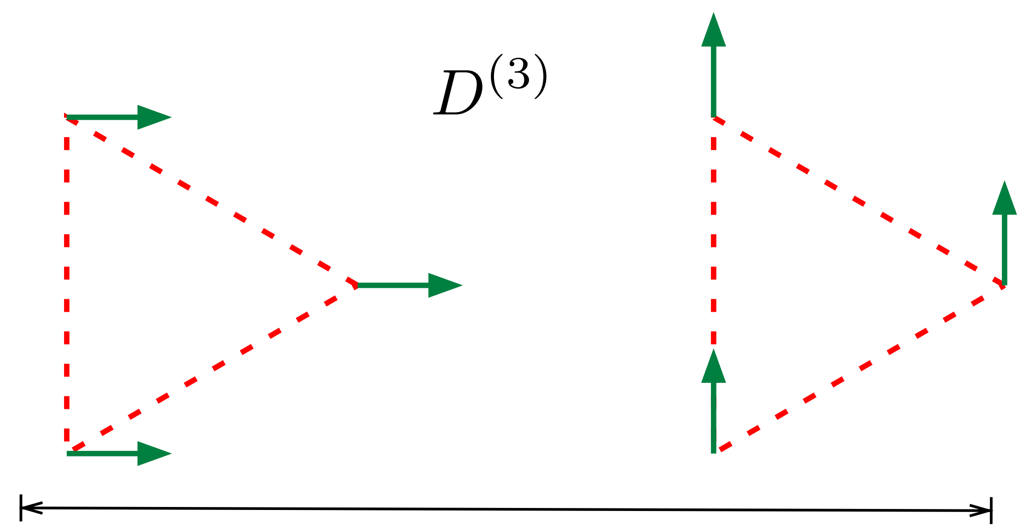


Zero Modes

$D^{(2)}$



$D^{(3)}$

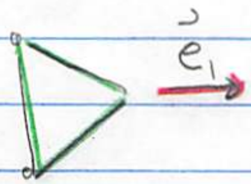


Constructing Vectors of Definite Symmetry

- Given a basis $\vec{e}_1, \vec{e}_2, \dots \vec{e}_6$

We can systematically construct vectors of definite symmetry. Take $\vec{e}_1$

$$\vec{e}_1 = (\hat{x}, \vec{0}, \vec{0}) = (1,0,\ 0,0,\ 0,0)$$



after we are done with $\vec{e}_1$ we could start with $\vec{e}_2$ etc.

- Then we have the projection operators

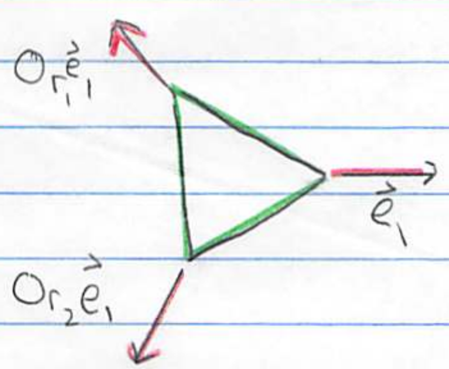
$$\mathbb{1} = \sum_{\mu, a} \hat{e}^{(\mu)}_{aa} \qquad\qquad \hat{e}^{(\mu)}_{aa} = \frac{n_\mu}{n_G} \sum_g (D^{(\mu)}_{aa}(g))^* \hat{O}_g$$

or

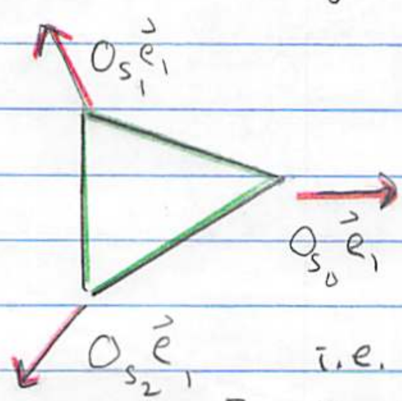
$$\vec{e}_1 = \sum_{\mu, a} \hat{e}^{(\mu)}_{aa} \vec{e}_1 = \sum_{a, \mu} \vec{e}^{(\mu)}_{aa,1}$$

these are the vectors in the a-th row of rep (μ) generated by $\vec{e}_1$

- Take a look at the effect of $O_g \vec{e}_1$:



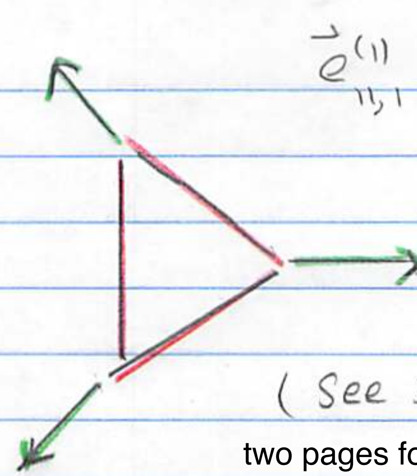
and



Picture

i.e. the image of $\vec{e}_1$ under reflection $\hat{S}_2$

Then



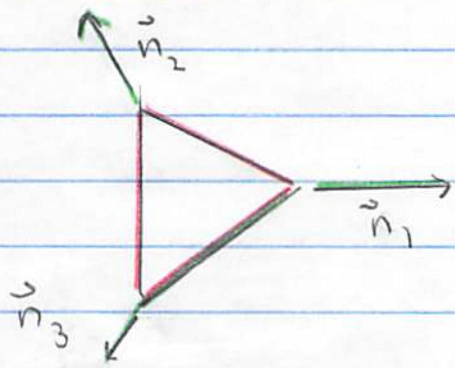
(1) $$\vec{e}^{(1)}_{11,1} = \frac{1}{6} \sum_g O_g \vec{e}_1$$

$$\vec{e}^{(1)}_{11,1} = \underline{\underline{\frac{2}{6} \left(\vec{n}_1, \vec{n}_2, \vec{n}_3 \right)}} \equiv \vec{\Psi}^{(1)}_{V}$$

(See slides!)

two pages forward

Where here and below we define the vectors



$\vec{n}_1 \equiv (1, 0)$

$\vec{n}_2 \equiv (-1/2, \sqrt{3}/2)$

$n_3 \equiv (-1/2, -\sqrt{3}/2)$

This must be an $\underline{\text{eigen-mode } \vec{e}^{(1)}_{11,1} \equiv \vec{\Psi}^{(1)}_{V}}$ since there is only one vector transforming as $D^{(1)}$.

(2) $$\vec{e}^{(2)}_{11,1} = \frac{1}{6} \left(\vec{e}_1 + O_{r_1}\vec{e}_1 + O_{r_2}\vec{e}_1 - O_{s_0}\vec{e}_1 - O_{s_1}\vec{e}_1 - O_{s_2}\vec{e}_1 \right)$$

these cancel for instance

$$= \vec{0}$$ see picture on previous page

(3) Now

$$\vec{e}^{(3)}_{11,1} = \frac{2}{6} \left(O_{\mathbb{1}} - \tfrac{1}{2} O_{r_1} - \tfrac{1}{2} O_{r_2} + O_{s_0} - \tfrac{1}{2} O_{s_1} - \tfrac{1}{2} O_{s_2} \right) \vec{e}_1$$

$$= \frac{4}{6} \left(\vec{n}_1, -\frac{1}{2}\vec{n}_2, -\frac{1}{2}\vec{n}_3 \right)$$ (see slides!)

See slides two pages forward

(4) $\vec{e}^{\,(3)}_{22,1} = \frac{2}{6}\left(O_{\mathbb{1}} - \frac{1}{2}O_{r_1} - \frac{1}{2}O_{r_2} - O_{s_0} + \frac{1}{2}O_{s_1} + \frac{1}{2}O_{s_2}\right)\vec{e}_1$

$= \vec{0}$ (Just thick about it graphichally)
see picture two pages back

- Associated by group ops with $\vec{e}^{\,(3)}_{11,1}$ and $\vec{e}^{\,(3)}_{22,1}$ are the vectors $\vec{e}^{\,(3)}_{21,1}$ and $\vec{e}^{\,(3)}_{12,1}$. Indeed, we said that these vectors can be obtained by linear combos of group ops acting on $\vec{e}^{\,(3)}_{11,1}$ and $\vec{e}^{\,(3)}_{21,1}$. • So, $\vec{e}^{\,(3)}_{12,1} = \vec{0}$ but $\vec{e}^{\,(3)}_{21,1}$ is the partner of $\vec{e}^{\,(3)}_{11,1}$

$$\vec{e}^{\,(3)}_{21,1} = \frac{2}{6}\left(0 + \frac{\sqrt{3}}{2}O_{r_1} - \frac{\sqrt{3}}{2}O_{r_1} + 0 + \frac{\sqrt{3}}{2}O_{s_1} - \frac{\sqrt{3}}{2}O_{s_2}\right)\vec{e}_1$$

$$= \frac{4}{6}\left(0, \frac{\sqrt{3}}{2}\vec{n}_1, -\frac{\sqrt{3}}{2}\vec{n}_2\right)$$ (see slides!)

See slide one page forward

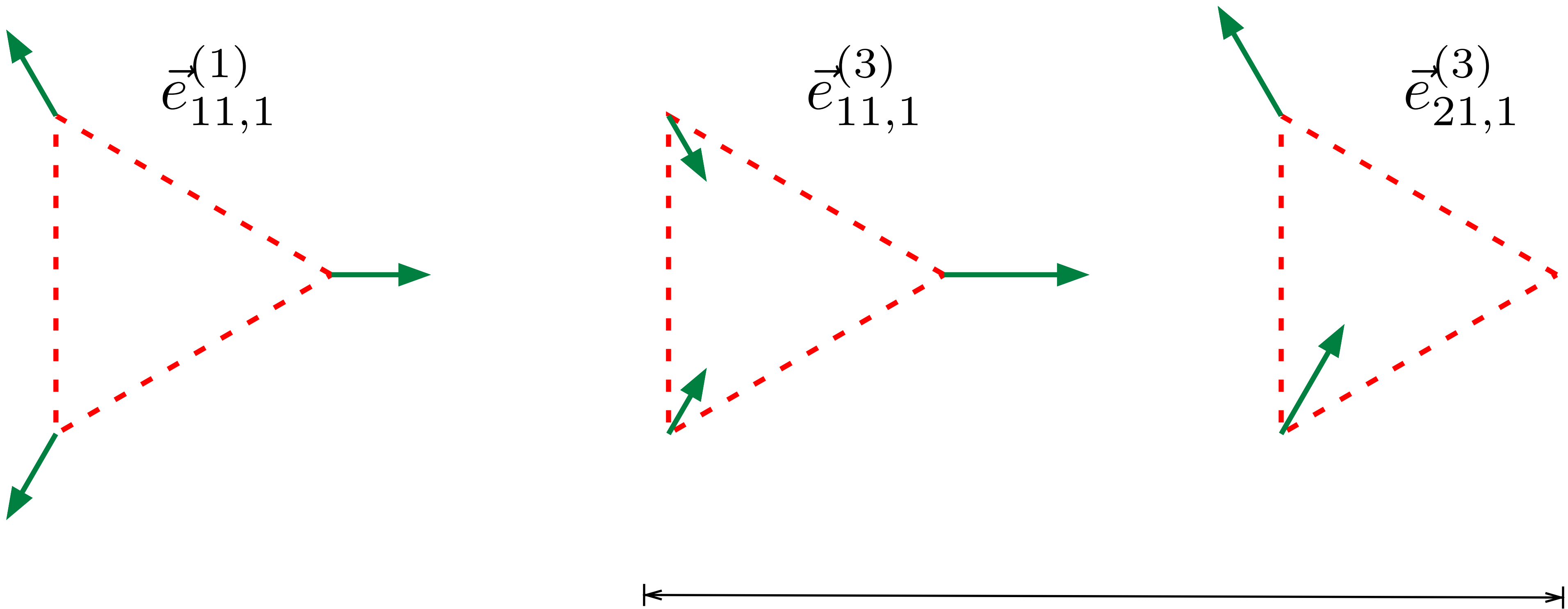
Summary:

- We decomposed $\vec{e}_1 = \vec{e}^{\,(1)}_{11,1} + \vec{e}^{\,(3)}_{11,1} = (\vec{n}_1, \vec{0}, \vec{0})$ check me ☺
  and associated partners $\vec{e}^{\,(3)}_{21,1}$

  These are shown on the next page

- We should no go on to $\vec{e}_2 \ldots \vec{e}_6$ do the same thing. This procedure will produce a complete symmetry adapted basis

Three vectors in the space



Partners in the $D^{(3)}$ irreducible rep

The Potential energy matrix will take the form

$$H = \begin{pmatrix} \underset{D^{(1)}}{\boxed{1\times 1}} & & & \\ & \underset{D^{(2)}}{\boxed{1\times 1}} & & \\ & & \boxed{2\times 2} & \\ & & & \boxed{2\times 2} \end{pmatrix}$$

first rows $D^{(3)}$

second rows of $D^{(3)}$ e.g. $\{\vec{e}^{\,(3)}_{21}, \vec{\phi}^{(3)}_2\}$

The $\boxed{2\times 2}$ and $\boxed{2\times 2}$ are same, Why?

- Since the is only one vector in $D^{(1)}$ ($D^{(1)}$ appears once in the decomposition $O_g = D^{(1)} \oplus D^{(2)} \oplus 2D^{(3)}$) we know that

$$\vec{\psi}^{(1)}_v \equiv \vec{e}^{\,(1)}_{11,1} \quad \text{is an eigen-vector}$$

- But $\{\vec{e}^{\,(3)}_{11,1}, \vec{e}^{\,(3)}_{21,1}\}$ are just basis elements. We should find two more $\{\vec{\phi}^{(3)}_1, \vec{\phi}^{(3)}_2\}$ then one eigenvector will lie in the span of

for instance $\{\vec{e}^{\,(3)}_{12,2}, \vec{e}^{\,(3)}_{22,2}\}$ will work

$$\{\vec{e}^{\,(3)}_{11,1}, \vec{\phi}^{(3)}_1\}$$

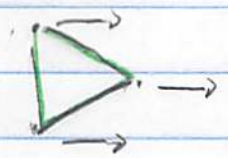
And another in the span of

$$\{\vec{e}^{\,(3)}_{21,1}, \vec{\phi}^{(3)}_2\}$$

In fact we know three eigen-vectors (zero modes) for free as we turn to next. But in general, one would need to diagonalize the 2x2 blocks to find the e-vects.

Zero Modes

- If we shift the whole molecule to the right we do not change the energy Similarly for up and down

$\bullet\!\Rightarrow \; \equiv$   $\equiv \; \Uparrow$

So the depicted vectors must be eigen-vectors

$\Rightarrow \; \equiv \vec{\psi}^{(3)}_{0x} = (1,0,1,0,1,0)$ $\qquad$ $\vec{\psi}^{(3)}_{0y} = (0,1,0,1,0,1) \equiv \Uparrow$

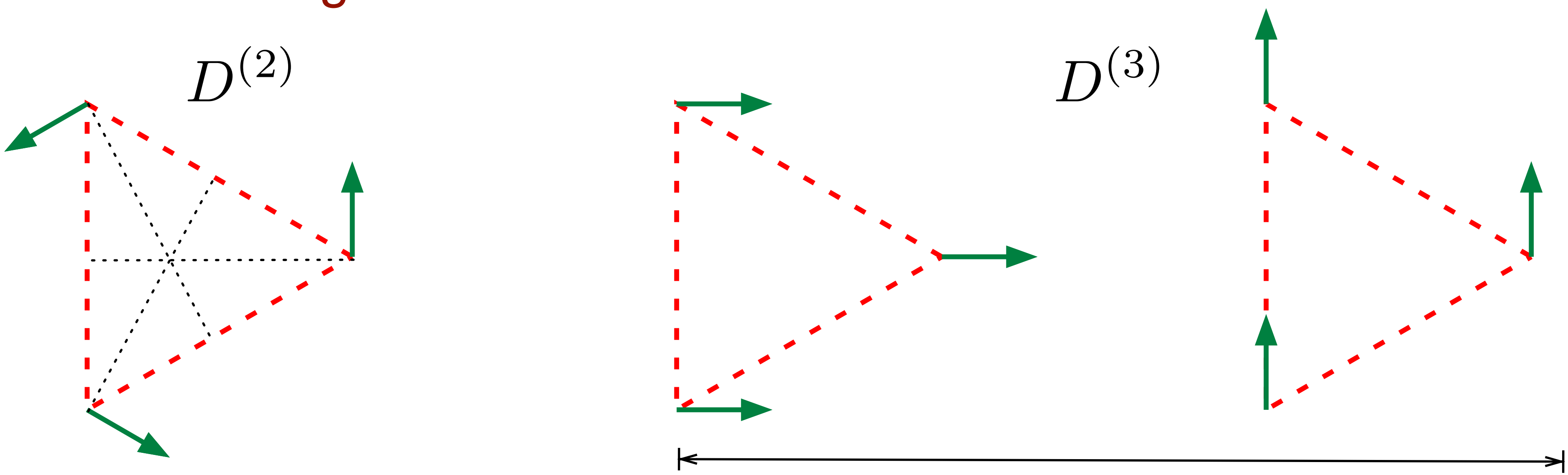
They are also partners in a $D^{(3)}$ rep. Since if I rotate $\vec{\psi}^{(3)}_{0x}$ by $2\pi/3$

$O_{G_1} \; \bullet\!\Rightarrow \; =$  $= -\frac{1}{2} \Rightarrow + \frac{\sqrt{3}}{2} \Uparrow$

I get back a combo of $\vec{\psi}^{(3)}_{0x}$ and $\vec{\psi}^{(3)}_{0y}$

- These are eigen-vectors. we should find the components of $\vec{e}^{(3)}_{11,1}$ and $\vec{e}^{(3)}_{21,3}$ which are orthogonal to these. This amounts to subtracting the center of mass motion of $\vec{e}^{(3)}_{11,1}$ and $\vec{e}^{(3)}_{21,1}$

Zero Mode Eigenvectors



$$\vec{\psi}^{(3)}_{1v} = \vec{e}^{(3)}_{11,1} - \frac{2}{6}\vec{\psi}^{(3)}_{0x}$$

chosen so $\vec{\psi}_{1v}$ has no center of mass motion in x-direction (see picture!)

On the next page

$$\vec{\psi}_{1v} = \frac{2}{6}\left((1,0), \left(-\frac{1}{2}, -\frac{\sqrt{3}}{2}\right), \left(-\frac{1}{2}, \frac{\sqrt{3}}{2}\right)\right)$$

$$\vec{\psi}^{(3)}_{2v} = \vec{e}^{(3)}_{21,1} - \frac{2}{6}\vec{\psi}^{(3)}_{0y}$$

2/6 chosen so no net y-motion (see pictrure!)

On the next page

- Then $\vec{\psi}^{(3)}_{1v}, \vec{\psi}^{(3)}_{2v}$ must be eigen vectors since it is a row of $D^{(3)}$ and orthogonal to $\vec{\psi}^{(3)}_{0x}, \psi^{(3)}_{0y}$

- There is one more zero eigenmode mode, obtained by rotating the molecule as a whole. Under a small rotation around the z axis the equilibrium position is modified $\vec{r}_{0i} \to \vec{r}_{0i} + \delta\vec{\theta} \times \vec{r}_{0i}$ (think $\delta\vec{r}_{0i} = \vec{\omega} \times \vec{r}_{01}\, \delta t$). For rotations around z:

$$\psi^{(2)}_{0r} \propto (\delta\vec{r}_{01}, \delta\vec{r}_{02}, \delta\vec{r}_{03})$$

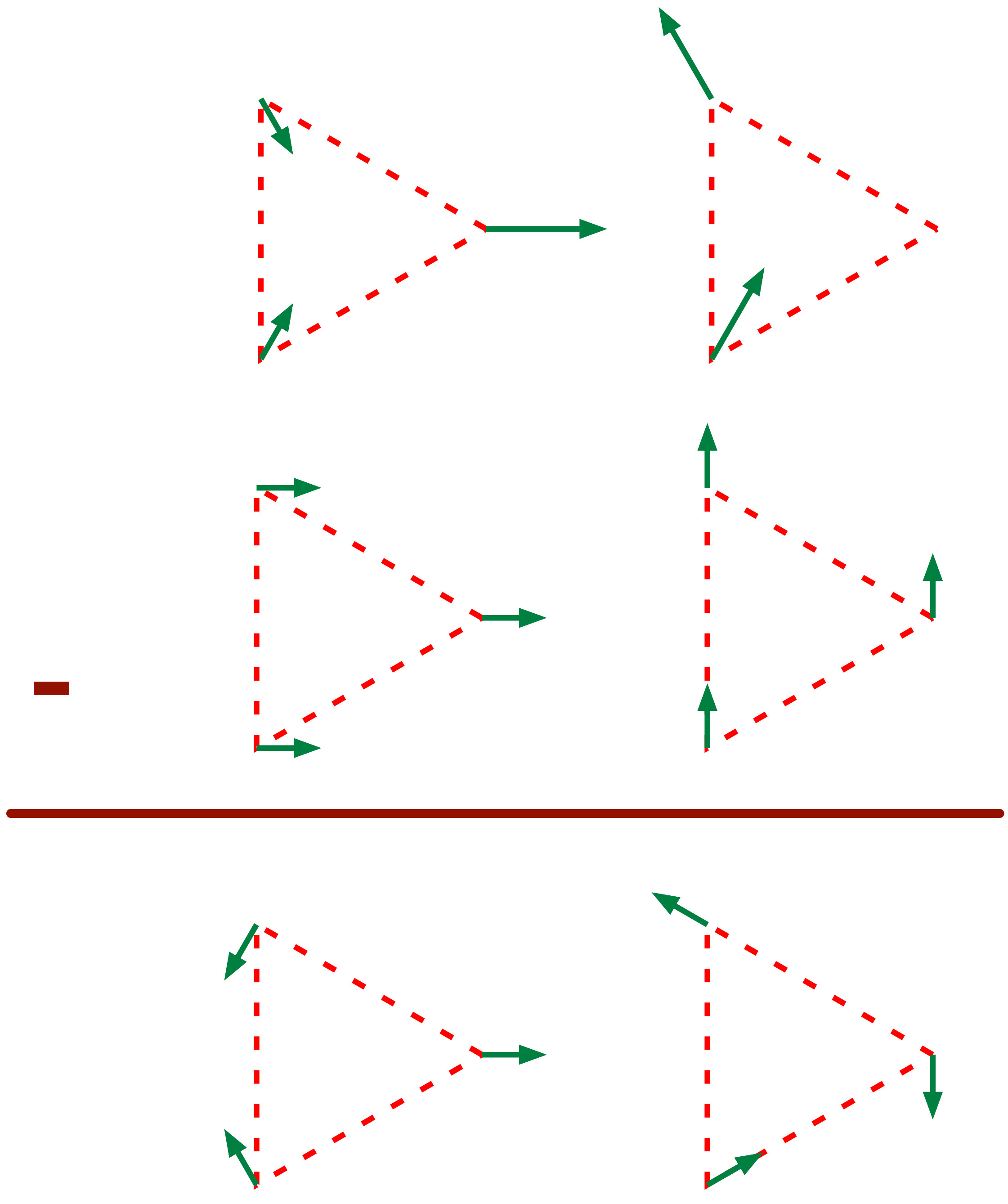
where $\delta\vec{r}_{01} = (0,1) = \hat{y}$

$\hat{y} = \hat{z} \times \hat{x}$

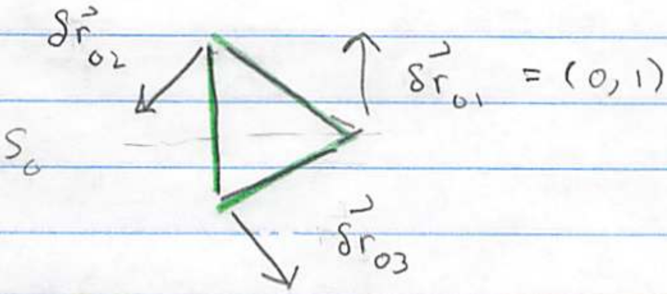
See picture on next page

(Actually it is one page back)

Subtracting Center of Mass Motion or Zero Modes



Where

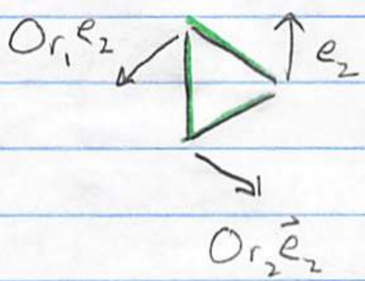


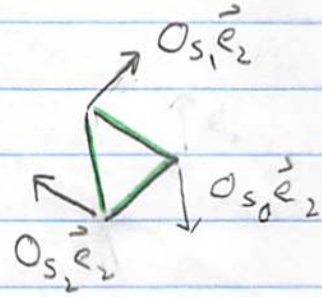
see picture

- A rotation acting on $\psi_{0R}^{(2)}$ yields $\psi_{0R}^{(2)}$, i.e. $O_{r_1}\vec{\psi}_{0r}^{(2)} = \vec{\psi}_{0r}^{(2)}$ while a reflection yields $-\vec{\psi}_{0r}^{(2)}$, i.e. $O_{S_0}\psi_{0r} = -\psi_{0r}$. Thus $\vec{\psi}_{0r}$ transforms as $D^{(2)}$.

- In fact it is easy to show that $\vec{\psi}_{0r}^{(2)} = \hat{e}_{11}^{(2)} \cdot \vec{e}_2$

$$\vec{\psi}_{0r} = \frac{1}{6}\left(O_{\mathbb{1}} + O_{r_1} + O_{r_2} - O_{S_0} - O_{S_1} - O_{S_2}\right)\vec{e}_2$$



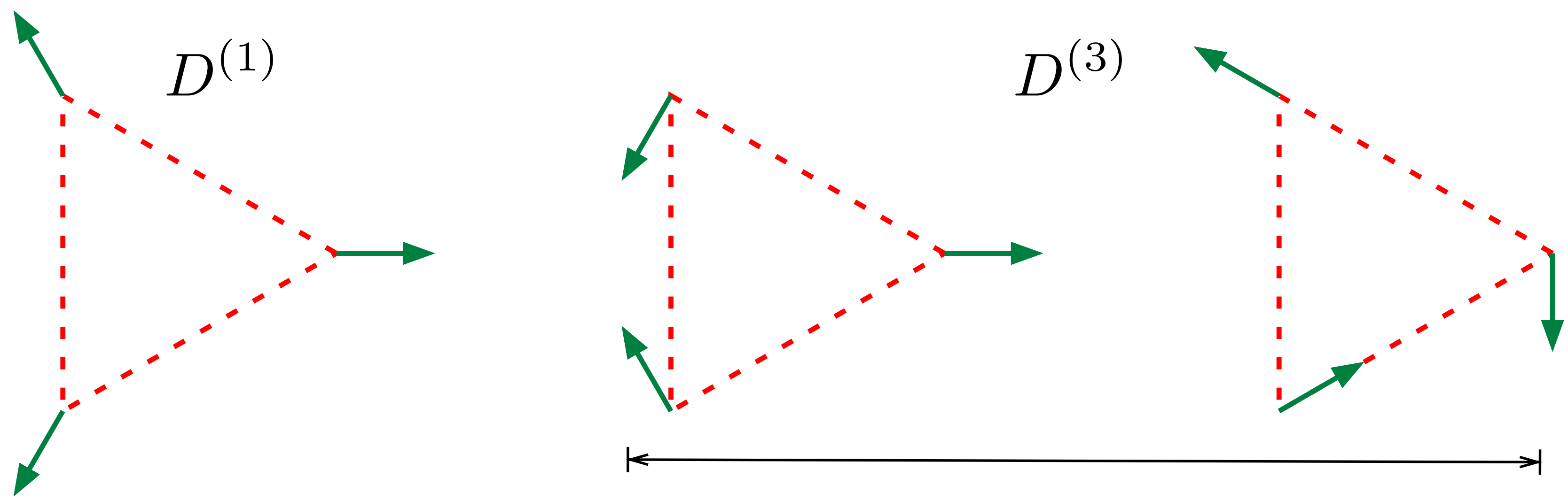


Summary · See Picture

3 Vibrational Eigenmode: $\vec{\psi}_V^{(1)}$, $\vec{\psi}_{1V}^{(3)}$, $\vec{\psi}_{2V}^{(3)}$

3 Zero Eigenmodes: $\vec{\psi}_{0r}^{(2)}$, $\vec{\psi}_{0x}^{(3)}$, $\vec{\psi}_{0y}$

Vibrational Modes



Zero Modes