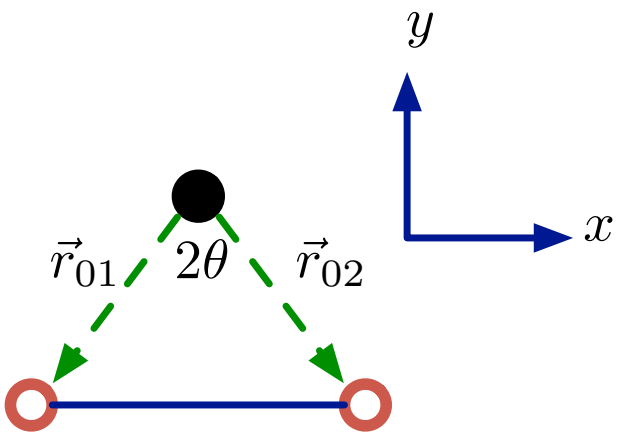
Problem 1. Classical Oscillations of H_2O

Consider a classical description H_2O. The oxygen is sufficiently heavy that it may be considered fixed. The hydrogen atoms are free to move in the three dimensional space. Their equilibrium positions relative to the oxygen are $\boldsymbol{r}_{01}$ and $\boldsymbol{r}_{02}$. These vectors have magnitude r_o and opening angle angle 2θ as shown below. Thus the full space of vibrations is characterized by the generalized vector

$$\begin{aligned} \boldsymbol{q} =& (x_1, y_1, z_1, x_2, y_2, z_2) && (1) \\ \equiv& (\boldsymbol{r}_1, \boldsymbol{r}_2) && (2) \end{aligned}$$

where $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are the displacements of the hydrogen from their equilibrium positions



The potential energy is a function of these oordinates. As a model take the potential

$$U = \frac{1}{2}k(\hat{\boldsymbol{r}}_{01} \cdot \boldsymbol{r}_1)^2 + \frac{1}{2}k(\hat{\boldsymbol{r}}_{02} \cdot \boldsymbol{r}_2)^2 + \frac{1}{2}k(x_1 - x_2)^2 \tag{3}$$

where $\hat{\boldsymbol{r}}_{0i}$ are unit vectors in the direction of $\boldsymbol{r}_{0i}$. The $(\hat{\boldsymbol{r}}_{0i} \cdot \boldsymbol{r}_1)^2$ terms describe interaction between the hydrogen and oxygen, while the remaining term describes the interactions between the hydrogen atoms.

The molecule has a symmetry group known as C_{2v} with group elements e, a, b, ab. Here e is the indentity element, a denotes a rotation by π about the y axis passing through the oxygen atom, b detenotes a reflection in the plane yz plane passing through oxygen, and ab denotes the rotation-reflection that is the combined operation

(a) Determine the 4×4 group multiplication table.

(b) What are the conjugacy classes. Show that for an abelian group the number of representations is equal to the order of the group.

Using Schur's lemma, show that all representations are one dimensional.

(c) Determine the character table of the C_{2v} by guess and check[1]: Check row orthogonality of characters and column orthogonality of charactersk. Check that the sum of characters squared is the order of the group. Use the constraints of part (b).

(d) Show that the group operations are represented on the state $\boldsymbol{q}$ through the matrices

$$O(a) = \begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \end{pmatrix} \tag{5}$$

$$O(e) = \text{figure me out} \tag{6}$$

$$O(b) = \text{figure me out} \tag{7}$$

$$O(ab) = \text{figure me out} \tag{8}$$

And deduce the characters $\chi(e) = 6$, $\chi(a) = 0$, $\chi(b) = 0$, $\chi(ab) = 2$.

(e) Show that the matrix representation $O(g)$ can be written (after a change of basis $O_{ab} \to \underline{O}_{ab}$) as

$$\underline{O}_{ab}(g) = 2D^{(1)} \oplus D^{(2)} \oplus D^{(3)} \oplus 2D^{(4)} \tag{9}$$

by using character analysis

(f) Given the first three basis vectors $\vec{\phi}_i$

$$\vec{\phi}_1 = (1, 0, 0, 0, 0, 0) \tag{10}$$

$$\vec{\phi}_2 = (0, 1, 0, 0, 0, 0) \tag{11}$$

$$\vec{\phi}_3 = (0, 0, 1, 0, 0, 0) \tag{12}$$

Decompose each $\vec{\phi}_i$ into vectors into transforming as a representation of the group C_{2v} using the projection operators $\hat{e}^{\mu}_{aa}$

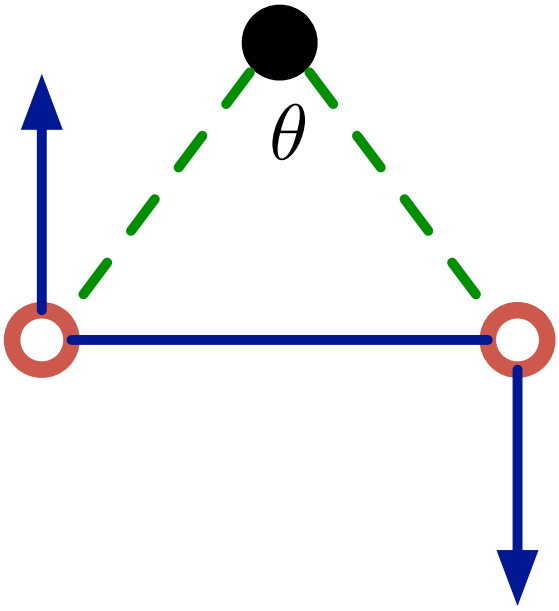
$$\vec{\phi}_i = \sum_{a,\mu} \vec{\phi}^{(\mu)}_{i,aa} \tag{13}$$

(For simplicity we will supress the aa label, since $a = 1$ for one dimensional "matrix" representations of this group, $\vec{\phi}^{\mu}_{i,aa} \equiv \vec{\phi}^{(\mu)}_i$.) Not all the $\vec{\phi}^{(\mu)}_i$ will be non-zero. You should find six linearly independent basis elements. Sketch these. For instance, a sketch of $\vec{\phi}^{(4)}_2$ is shown below. There are several advantages of this basis over the original $\vec{\phi}_i$ with $i = 1 \ldots 6$.

[1]

	e	a	b	ab
A_1 $\mu = 1$	1	1	1	1
A_2 $\mu = 2$	1	1	- 1	-1
B_1 $\mu = 3$	1	-1	1	-1
B_2 $\mu = 4$	1	-1	-1	1

(4)



(g) Three vectors in the span of this basis are "zero eigenmodes" of the potential matrix $\mathcal{H}$. They are obtained by rotating the molecule as a whole by a small amount $\delta\theta$. They do not change the potential energy of the molecule, and do not correspond to actual vibrations of the molecule that cost energy to establish.

For instance, if we displace one hydrogen atom slightly in the positive z direction and the other hydrogen slightly in the negative z direction, this is just a small rotation as a whole around the z axis.

Now we formalize this concept. If the equilibrium position of the hdrogen molecules is $\vec{r}_{0i}$ relative to the center of mass, then a small rotation by an amount $\delta\theta$ around the $\boldsymbol{n}$ axis produces a shift of the coordinates:

$$\delta\vec{r}_{0i} = \delta\theta\,\vec{n} \times \vec{r}_{0i} \tag{14}$$

If we take $\vec{n}$ in the $\hat{\mathbf{y}}$ direction we have

$$\delta\vec{r}_{01} = \delta\theta\, r_0 \sin(\theta)\ (0,0,1) \tag{15}$$
$$\delta\vec{r}_{02} = \delta\theta\, r_0 \sin(\theta)\ (0,0,-1) \tag{16}$$

Corresponding to a zero eigen-mode[2]

$$\vec{\psi}_{0,y} = (0,0,1,0,0,-1) \tag{17}$$

(i) Determine the zero eigenmodes, $\vec{\psi}_{0,x}, \vec{\psi}_{0,y}, \vec{\psi}_{0,z}$ associated with rotations around the x, y, and z axes.

[2]We use $\vec{\psi}$ instead of $\vec{\phi}$ because it is an eigenvector as you will show below. Without further analysis it is not clear that the $\vec{\phi}_i^{(\mu)}$ are eigenvects:

(ii) Show that the bais elements $\vec{\phi}_3^{(2)}$ and $\vec{\phi}_3^{(3)}$ are each proportional to a single zero mode in the set, $\vec{\psi}_{0,x}, \vec{\psi}_{0,y}, \vec{\psi}_{0,z}$.

(h) Consider the two span of two basis vectors $\vec{\phi}_1^{(4)}$ and $\vec{\phi}_2^{(4)}$. A linear combination of these two vectors corresponds to a zero mode. Determine this combination. Explictly show that it is a zero mode of $\mathcal{H}$ by evaluating $\mathcal{H}\,\vec{\psi}$

Determine the vector component of $\vec{\phi}_1^{(4)}$ (or $\vec{\phi}_2^{(4)}$) which is orthogonal to the zero mode and sketch it. Let us call this vector $\vec{\psi}_1^{(4)}$ since as we will see it is an eigen vector.

(i) Consider basis elements of definite symmetry $\vec{\phi}_a^{(\mu)}$. Using group theoretical arguements the next problem establishes that

$$\left(\vec{\phi}_a^{\mu}, \mathcal{H}\vec{\phi}_b^{\nu}\right) \propto \delta_{ab}\delta_{\mu\nu} \tag{18}$$

Since there is only one basis element belonging to $D^{(4)}$, namely $\vec{\psi}_1^{(4)}$. It must therefore be an eigenvector of $\mathcal{H}$. Determine the associated oscillation frequency with this eigenvector.

(j) Symmetry can only take you so far. There are two basis elements belonging to $D^{(1)}$, namely $\vec{\phi}_1^{(1)}$ and $\vec{\phi}_2^{(1)}$. The eigen modes $\mathcal{H}$ of the system will lie in the span of these two basis elements. This reduces the problem of finding the eigen-modes to diagonlizing the 2×2 matrix. Write down the normal mode problem in this basis and deduce the eigen frequencies.

Problem 2. Inner product

For definiteness consider the canonical D_3 (or triangle) group that we discussed in class in two spatial dimensions. Take a inner product of two functions as simply

$$\langle f, h\rangle = \int d^2\boldsymbol{x}\, f^*(\boldsymbol{x})\, h(\boldsymbol{x}) \tag{19}$$

For example $f(\boldsymbol{x})$ might be $f(\boldsymbol{x}) = \exp(-x^2-y^2)$ and $h(\boldsymbol{x}) = \exp(-x^2-(y-3)^2)$. It is clear that if we rotate both of these functions by $2\pi/3$ and compute their inner product again we will get the same answer

(a) Prove this statement, i.e. prove

$$\langle O_{r_1} f, O_{r_1} h\rangle = \langle f, h\rangle \tag{20}$$

We say that the inner product is invariant under the operations of the group if

$$\langle O_g f, O_g h\rangle = \langle f, h\rangle \tag{21}$$

for all elements of the group.

(b) Let $f_a^{(\mu)}(\boldsymbol{x})$ transform as a row (i.e. row a) of an irreducible representation (i.e. representation (μ)) of the group, i.e.

$$O_g f_a^{(\mu)}(\boldsymbol{x}) = f_b^{\mu}(\boldsymbol{x}) D_{ba}^{(\mu)}(g) \tag{22}$$

Use part (a) to show that

$$\left\langle f_a^{(\mu)}, f_b^{(\nu)} \right\rangle = C^{(\mu)} \delta_{\mu\nu}\delta_{ab} \tag{23}$$

where the coefficient $C^{(\mu)}$ is independent of row, but does depend on the representation. Express $C^{(\mu)}$ using inner products of $f_a^{(\mu)}$.

Use the "colorful" slides from class to heuristically explain this result.

(c) Let the Hamiltonian $\mathcal{H}$ commute with the operators of the group

$$O_g \mathcal{H} O_g^{-1} = \mathcal{H} \tag{24}$$

Show that

$$\left\langle f_a^{(\mu)}, \mathcal{H} f_b^{(\nu)} \right\rangle = h^{(\mu)} \delta_{\mu\nu}\delta_{ab} \tag{25}$$

where h^{μ} is independent of a. Express $h^{(\mu)}$ using inner products of $f_a^{(\mu)}$ and $\mathcal{H}$.