Vibrational spectrum of H_2O

n degrees of freedom

$$H = \frac{1}{2}\dot{x}^T M \dot{x} - \frac{1}{2} x^T V x$$

symmetric n×n matrices

eqs of motion $M\ddot{x} = Vx$

solutions $x(t) \sim e^{i\omega_k t} x$

$$\Rightarrow \; -\omega_k^2 M x_k = V x_k$$

ω_k are the normal mode frequencies given by $\det(V - \omega^2 M) = 0$

$$\omega_k = \omega_l \Rightarrow x_k^T M y_l = 0$$

inner product $(x\, M\, y)$

equilibrium configuration has symmetry G then $x \to D(g)\,x$

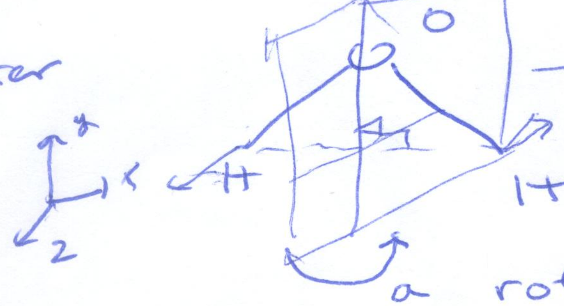
$D(g)$ is n dimensional representation

Symmetry should leave the quadratic form invariant $\Rightarrow$

$$D(g)^T M D(g) = M$$

$$D(g)^T V D(g) = V$$

$\Rightarrow$ $D(g)x_i$ and x_i satisfy the same eigenvalue equation water



b is reflectio through this plane

a rotation by π

ab is a reflection in the plane of O and the two H's

$a^2 = e \qquad b^2 = e \qquad ab = ba$

$(ab)^2 = e$

character table of symmetry group

	e	a	b	ab
1	1	1	1	1
χ_2	1	1	-1	-1
χ_3	1	-1	1	-1
χ_4	1	-1	-1	1

ablian group $\Rightarrow$ all irreps are 1d because each element is a conjugacy class

$$\left.\begin{aligned} \sum_{k=1}^{4} \chi_k^2(g) &= 4 \\ \sum_{g} \chi_k^2(g) &= 4 \end{aligned}\right\} \Rightarrow \chi_k(g) = \pm 1$$

should be orthogonal to 1 1 1 1

$\Rightarrow$ we have two -1 in each row

$\Rightarrow$ only 1 extra 1, this gives 3 possibilities

Next we consider the effect of the representation on the small displacements

$$\vec{x} = (x_0, y_0, z_0, x_{H_1}, y_{H_1}, z_{H_1}, x_{H_2} y_{H_2}, z_{H_2})$$

$$D(a)\vec{x} = (-x_0, y_0, -z_0, -x_{H_2}, y_{H_2}, -z_{H_2}, -x_{H_1}, y_{H_1}, -z_{H_1})$$

$$D(b)\vec{x} = (-x_0\ y_0\ z_0.\ -x_{H_2}\ y_{H_2}\ z_{H_2} - x_{H_1}, y_{H_1}\ z_{H_1})$$

$$D_{ab}(x) = (x_0\ y_0 - z_0\quad x_{H_1}\ y_{H_1} - z_{H_1}\ x_{H_2}\ y_{H_2} - z_{H_2}$$

$$\chi^D(e) = 9$$

$$\chi^D(a) = -1$$

$$\chi^D(b) = 1$$

$$\chi^D(ab) = 3$$

atoms that are interchanged do not contribute to the trace.

we can decompose this representation into irreducible representation. by taking scalar products

$$\frac{1}{4}\begin{pmatrix} 9 \\ -1 \\ 1 \\ 3 \end{pmatrix}\begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} = 3, \quad \frac{1}{4}\begin{pmatrix} 9 \\ -1 \\ 1 \\ 3 \end{pmatrix}\begin{pmatrix} 1 \\ 1 \\ -1 \\ -1 \end{pmatrix} = 1$$

$$\Rightarrow \chi_D = 3\chi_1 + \chi_2 + 2\chi_3 + 3\chi_4$$

How do the symmetries act when the motion is a translation?

$T_x \rightarrow \quad X_{T_x} = (\alpha, 0, 0, \alpha, 0, 0, \alpha\, 0\, 0)$

$D(a)\, X_{T_x} = -X_{T_x}$

$D(b)\, X_{T_x} = -X_{T_x}$ This is D_4

$D(ab)\, X_{T_x} = X_{T_x}$

$T_y \quad X_{T_y} = (0, \alpha, 0, 0\, \alpha\, 0 \quad 0\, \alpha\, 0)$

$D(a)\, X_{T_y} = X_{T_y}$

$D(b)\, X_{T_y} = X_{T_y}$ This is D_1

$D_{ab}\, X_{T_y} = X_{T_y}$

$T_z \quad X_{T_z} = (0\, 0\, \alpha\;\; 0\, 0\, \alpha\;\; 0\, 0\, \alpha)$

$D(a)\, X_{T_z} = -X_{T_z}$

$D(b)\, X_{T_z} = X_{T_z}$ This is D_3

$D(ab)\, X_{T_z} = -X_{T_z}$

Rotation about y-axis through O

O remains in place

$z_{H_1} = R \sin\phi \qquad z_{H_2} = -R\sin\phi$

$x_{H_1} = R(1-\cos\phi) \qquad x_{H_2} = -R(1-\cos\phi)$

Under the symmetry representation this motion behaves as

$D(a)\, X = (0, 0, 0, R(1-\cos\phi), 0, +R\sin\phi, -R(1-\cos\phi, 0, -R\sin\phi)$

infinitesimal ϕ

$X = (0, 0\, 0,\; 0, 0, R\phi,\; 0\, 0 -R\phi)$

$D(a)\, X = X, \quad D(b)\, X = X \qquad D(ab)\, X = X$

This is D_2

Rotation about X axis of O

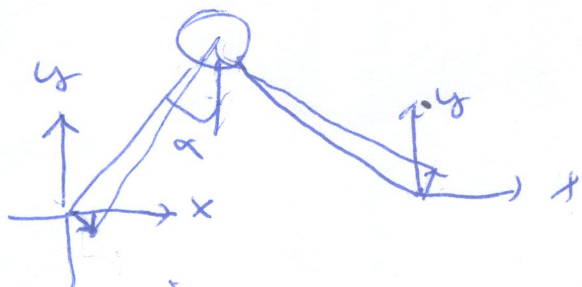
$z_{H_1} = z_{H_2} = R\phi$ infinitesimal

$D(a)\, X = -X$

$D(b)\, X = X$ this is $\cancel{B_1}$ D_3

$D(ab)\, X = -X$

Rotation about z axis trough O



$\delta x_{H_1} = R\phi \cos\alpha$ $\delta x_{H_2} = R\phi\cos\alpha$

$\delta y_{H_1} = -R\phi \sin\alpha$ $\delta y_{H_2} = R\phi \sin\alpha$

$X = (0, 0, 0, R\phi\cos\alpha, -R\phi\sin\alpha, 0,$
$R\phi\cos\alpha, R\phi\sin\alpha\ 0)$

$D(a)\, X = (0, 0, 0, -R\phi\cos\alpha, R\phi\sin\alpha, 0)$
$-R\phi\cos\alpha\ -R\phi\sin\alpha, 0)$

$= -X$

$(0, 0, 0, -R\phi\cos\alpha, R\phi\sin\alpha\ 0,$
$, -R\phi\cos\alpha, -R\phi\cos\alpha, 0)$

$D(b)\, X = 1$

$D(ab)\, X = X$

This D_4

So the zero modes are

translations $D_4 \quad D_1 \quad D_3$
rotations $D_2 \quad D_3 \quad D_4$

In total $D = 3\,D_1 + D_2 + 2\,D_3 + 3\,D_4$

$\Rightarrow$ vibration $2\,D_1 + D_4$

Projection on $\mathbb{1}$.

$$p^{D_1} = \frac{1}{4}\left(\chi^{D_1}(e)\,D(e) + \chi^{D_1} D(a) + \chi^{D_1} D(b) + \chi^{D_1}(ab)\,D(b)\right)$$

$$= \frac{1}{4}\left(D(e) + D(a) + D(b) + D(ab)\right)$$

This combination will have the character of D_1

$\mathrm{Tr}\, p^{D_1} \neq 0$ if $D = D_1$ otherwise it is zero

How does this combination act on a displacement in the x direction $\sigma_{H_1 x}$

$$p^{D_1}_{1}\; \sigma_{H_1 x} = \frac{1}{4}\left(\vec{\sigma}_{H_1 x} - \vec{\sigma}_{H_2 x} - \vec{\sigma}_{H_2 x} + \sigma_{H_1 x}\right)$$

$$= \frac{1}{2}\left(\vec{\sigma}_{H_1 x} - \vec{\sigma}_{H_2 x}\right)$$ if $\sigma_{H_1 x} = \alpha$ then $\sigma_{H_2 x} = \alpha$

$$p^{D_1}\; \sigma_{H_2 x} = \frac{1}{4}\left(\vec{\sigma}_{H_2 x} - \vec{\sigma}_{H_1} - \vec{\sigma}_{H_1 x} + \vec{\sigma}_{H_2 x}\right)$$

$$= \frac{1}{2}\left(\sigma_{H_2 x} - \vec{\sigma}_{H_1}\right)$$

$$\Rightarrow \quad p^{D_1}\left(\vec{\sigma}_{H_1 x} - \sigma_{H_2 x}\right) = \vec{\sigma}_{H_1 x} - \vec{\sigma}_{H_2 x}$$

P^{D_1} is one dimensional

$\Rightarrow$ this is the vibrational mode.

But we have two vibrational modes in D_1. To find the other one we look at a motion $\vec{v}_{H_1 y}$ an $\vec{v}_{Oy}$

$$P_1^{D_1}\ \vec{v}_{H_1 y} = \frac{1}{2}(\vec{v}_{H_1 y} + \vec{v}_{H_2 y})$$

$$P_1^{D_1}\ \vec{v}_{H_2 y} = \frac{1}{2}(\vec{v}_{H_1 y} + \vec{v}_{H_2 y})$$

$$P_1^{D_1}\ \vec{v}_{Oy} = \vec{v}_{Oy}$$

$$P^{D_1}\left(\alpha(\vec{v}_{H_1 y} + \vec{v}_{H_2 y}) + \beta\vec{v}_{Oy}\right) = \alpha(\vec{v}_{H_1 y} + \vec{v}_{H_2 y}) + \beta\vec{v}_{Oy}$$

Translation moves center of mass

center of mass mode

$\vec{v}_{H_1 y} = \vec{v}_{H_2 y}$ $\qquad \alpha = \frac{m_H}{2m_H + m_O} \quad \beta = \frac{m_O}{2m_H + m_O}$

vibrational mode is perpendicular to this

$\alpha = \frac{m_O}{2} \qquad \beta = -m_H$ leaves center of mass invariant

so $\vec{v}_{H_1 y} = \frac{m_O}{2}\vec{y}_1 \qquad \vec{v}_{H_2 y} = \frac{m_O}{2}\vec{y}_1 \qquad \vec{v}_O = -m_H\vec{y}$

$\Rightarrow m_H\vec{v}_{H_1} + m_H v_{H_2} + m_O v_O = m_O m_H \vec{y} \times 0$
$= 0$

$\Rightarrow \frac{\vec{v}_{H_1}}{\vec{v}_O} = -\frac{m_O}{2m_H}$

Finally we look at the representation D_4

$$P^{D_4} = \frac{1}{4}\left(\chi^{D_4}(e)\, D(e) + \chi^{D_4}(a)\, D(a) + \chi^{D_4}(b)\, D(b) + \chi^{D_4}(ab)\, D(ab) \right)$$

$$= \frac{1}{4}\left(D(e) - D(a) - D(b) + D(ab) \right)$$

When we decompose P^{D_4} in irreducible characters then it only contains the D_1^4 representation.

So it may contain rotations about the z axis and translations in the x direction

$$P^{D_4} : \vec{v}_{H_1 x} = (\vec{v}_{H_1 x} + \vec{v}_{H_2 x} + \vec{v}_{H_2 x} + \vec{v}_{H_1 x})$$
$$= \frac{1}{2}(\vec{v}_{H_1 x} + \vec{v}_{H_2 x})$$

$$P^{D_4}\ \vec{v}_{H_2 x} = \frac{1}{2}(v_{H_1 x} + v_{H_2 x})$$

$$P^{D_4}\ \vec{v}_{O x} = \vec{v}_{O x}$$

$$P^{D_4}\ \vec{v}_{H_1 y} = \frac{1}{2}(\vec{v}_{H_1 y} - \vec{v}_{H_2 y})$$

$$P^{D_4}\ \vec{v}_{H_2 y} = \frac{1}{2}(\vec{v}_{H_2 y} - \vec{v}_{H_1 y})$$

$$P^{D_4}\ \vec{v}_{O y} = 0$$

In the same way as the D_1 rep.
this contains a translational mode
in the x direction

$$P^{D_4}(\vec{v}_{H_1x}+\vec{v}_{H_2x}) = (\vec{v}_{H_1x}+\vec{v}_{H_2x})$$

$$P^{D_4}(\vec{v}_{H_1y}-\vec{v}_{H_2y}) = (\vec{v}_{H_1y}-\vec{v}_{2}{}_{H_2y})$$

$$a(\vec{v}_{H_1x}+\vec{v}_{H_2x}) + b(\vec{v}_{H_1y}-\vec{v}_{H_2y})$$

rotation if $a = R\phi\cos\alpha$
$b = -R\phi\sin\alpha$

and $\vec{v}_{H_1x} = \hat{x}_{H_1}$
$\vec{v}_{H_1y} = \hat{y}_{H_1}$
$\vec{v}_{H_2x} = \hat{x}_{H_2}$
$\vec{v}_{H_2y} = \hat{y}_{H_2}$

vibrational mode