Normal Coordinates [*]

[*]l2h:osc.tex

Consider two oscillators as shown. For simplicity, the two outer force constants are called

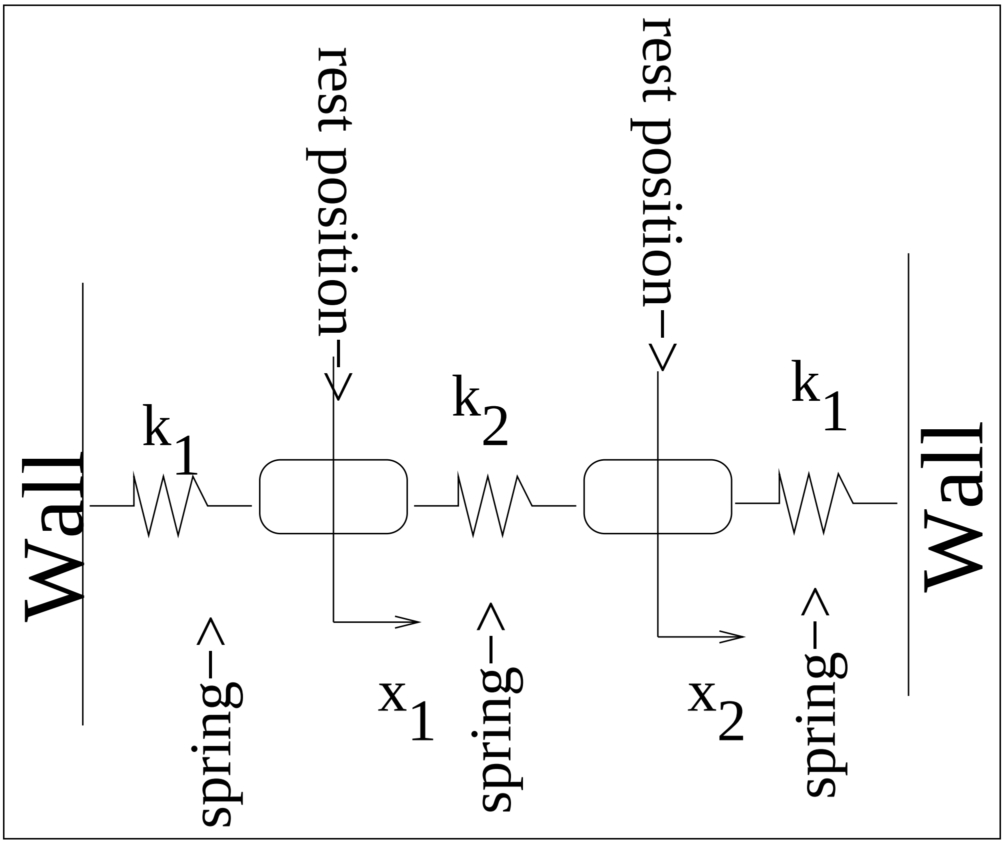

FIG. 1: Two masses, three springs, normal mode introduction

k_1 and the inner force constant is called k_2. Assume that the masses of both particles are the same. Then we have

$$m\ddot{x}_1 = -k_1 x_1 - k_2(x_1 - x_2)$$

$$m\ddot{x}_2 = -k_1 x_2 - k_2(x_2 - x_1)$$

and, defining ω as

$$\omega = \frac{k_1 + k_2}{m}$$

and

$$\Omega = \frac{k_2}{m}$$

we have

$$\ddot{x}_1 = -\omega^2 x_1 + \Omega^2 x_2 \tag{1}$$

$$\ddot{x}_2 = -\omega^2 x_2 + \Omega^2 x_1 \tag{2}$$

What if we tried to write this in matrix form as

$$\begin{pmatrix} \ddot{x}_1 \\ \ddot{x}_2 \end{pmatrix} = \begin{pmatrix} -\omega^2 & \Omega^2 \\ \Omega^2 & -\omega^2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

which we wish to rewrite in a particular manner, left multiplying by a matrix (A)

$$A \begin{pmatrix} \ddot{x}_1 \\ \ddot{x}_2 \end{pmatrix} = A \begin{pmatrix} -\omega^2 & \Omega^2 \\ \Omega^2 & -\omega^2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

$$A \begin{pmatrix} \ddot{x}_1 \\ \ddot{x}_2 \end{pmatrix} = A \begin{pmatrix} -\omega^2 & \Omega^2 \\ \Omega^2 & -\omega^2 \end{pmatrix} A^{-1} A \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

where we have inserted $A^{-1}A$ between the square matrix and the column vector, assuming that this product is the unit matrix. Now, the question is, is there a good choice for the matrix A?

And the answer is, yes, one that would produce a diagonal matrix multiplying the column vector, since this would *not intermix* the two elements of the column vector!

To produce this, we attempt to solve for the eigenvalues and eigenvectors of the original matrix, i.e.,

$$\begin{vmatrix} -\omega^2 - \lambda & \Omega^2 \\ \Omega^2 & -\omega^2 - \lambda \end{vmatrix} = 0$$

Expanding the determinant, we have

$$\left(-\omega^2 - \lambda\right)^2 = \Omega^2$$

which gives

$$\lambda = -\omega^2 \mp \Omega$$

i.e., there are two values of λ which are eigenvalues of the original matrix, so

$$A \begin{pmatrix} -\omega^2 - \lambda & \Omega^2 \\ \Omega^2 & -\omega^2 - \lambda \end{pmatrix} A^{-1} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix}$$

where the subscripts indicate which sign to use in the $\mp$. To solve for the transformation matrix, A, we need the eigenvectors associated with the aforedetermined eigenvalues. We have

$$\begin{pmatrix} -\omega^2 & \Omega^2 \\ \Omega^2 & -\omega^2 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \lambda_+ \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

which is

$$\begin{pmatrix} -\omega^2 & \Omega^2 \\ \Omega^2 & -\omega^2 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = -\omega^2 + \Omega^2 \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

and

$$\begin{pmatrix} -\omega^2 & \Omega^2 \\ \Omega^2 & -\omega^2 \end{pmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = -\omega^2 - \Omega^2 \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

so the A matrix is (in un-normalized form) so the A matrix is

$$\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

The λ_+ solution corresponds to a solution $x_1 + x_2$ while the other corresponds to $x_1 - x_2$.

Thus, there are two solutions which are "simple". Adding Equations 1 and 2 we obtain

$$\frac{d^2(x_1 + x_2)}{dt^2} = -\omega^2(x_1 + x_2) + \Omega^2(x_1 + x_2)$$

which is

$$\frac{d^2(x_1 + x_2)}{dt^2} = (-\omega^2 + \Omega^2)(x_1 + x_2)$$

which, of course, has as a solution

$$(x_1 + x_2) = K_1 \cos\sqrt{\omega^2 - \Omega^2}t + K_2 \sin\sqrt{\omega^2 - \Omega^2}t$$

(related to λ_+) which is simple harmonic motion. Likewise,

$$(x_1 - x_2) = K_3 \cos\sqrt{\omega^2 + \Omega^2}t + K_4 \sin\sqrt{\omega^2 + \Omega^2}t$$

(related to λ_-). These are the two normal modes of the coupled oscillators. There is a symmetric mode (+) and anti-symmetric mode (-).

I. WATER

(Note, this section is an amplification of a treatment due to G. M. Barrow, "Introduction to Molecular Spectroscopy", McGraw-Hill Book Co., New York, 1962) For a water molecule made up of $H_1 - O - H_2$, the kinetic energy of the molecule would be

$$T = \frac{1}{2}\left(m_H(\dot{x_{H_1}}^2 + \dot{y_{H_1}}^2) + m_H(\dot{x_{H_2}}^2 + \dot{y_{H_2}}^2) + m_O(\dot{x_O}^2 + \dot{y_O}^2)\right) \tag{3}$$

in Cartesian coördinates (where we have assumed a molecular x-y plane for convenience), and

$$V = \frac{1}{2}\left(k_{O-H_1}(\delta r_{O-H_1})^2 + k_{O-H_2}(\delta r_{O-H_2})^2 + k_{H-O-H}(\delta\theta)^2\right) \tag{4}$$

where δr is the deviation of r from its equilibrium value, and $\delta\theta$ is the deviation of θ (the H-O-H angle) from its normal value. These are 0.9584Åand 104.5^o, respectively. Parenthetically, $k_{O-H_1} = k_{O-H_2}$. Notice that the two kinds of energies are given in two different coördinate systems, making it necessary (usually) to choose one or the other for use in solving the problem. Alternatively, one could convert to yet a third coördinate system, one most convenient for solving the eventual problem, and convert both kinetic and potential energy into this final coördinate system. It is this latter strategy which is commonly employed, where the new coördinate system is the normal coördinate scheme!

We propose to use the standard "symmetry" coördinates S_i, with i running from 1 through 6. Of these 6 coördinates, 2 will correspond to translation in the x and y directions, and one will correspond to rotation, all three applied to the entire molecule. This will leave three of the S's which will correspond to the normal modes of internal vibration.

S_1, S_2, and S_3 are special definitions of normal modes which are shown (out of scale) here: For simplicity, the two outer force constants are called k_1 and the inner For simplicity, the two outer force constants are called k_1 and the inner One has

$$\dot{x}_{H_1} = \dot{S}_1 - \dot{S}_3 \sin\frac{\theta}{2} \tag{5}$$

$$\dot{y}_{H_1} = \dot{S}_2 - \dot{S}_3 \cos\frac{\theta}{2} \tag{6}$$

Squaring one obtains

$$\dot{x}_{H_1}^2 = \dot{S}_1^2 - 2\dot{S}_1\dot{S}_3 \sin\frac{\theta}{2} + \left(\dot{S}_3 \sin\frac{\theta}{2}\right)^2$$

$$\dot{y}_{H_1}^2 = \dot{S}_2^2 - 2\dot{S}_2\dot{S}_3 \cos\frac{\theta}{2} + \left(\dot{S}_3 \cos\frac{\theta}{2}\right)^2$$

and, defining

$$\dot{x}_O = \frac{2m_H\dot{S}_3 \sin\frac{\theta}{2}}{m_O} \tag{7}$$

$$\dot{y}_O = \frac{2m_H\dot{S}_2}{m_O} \tag{8}$$

and squaring these one obtains

$$\dot{x}_O^2 = \left(\frac{2m_H\dot{S}_3 \sin\frac{\theta}{2}}{m_O}\right)^2$$

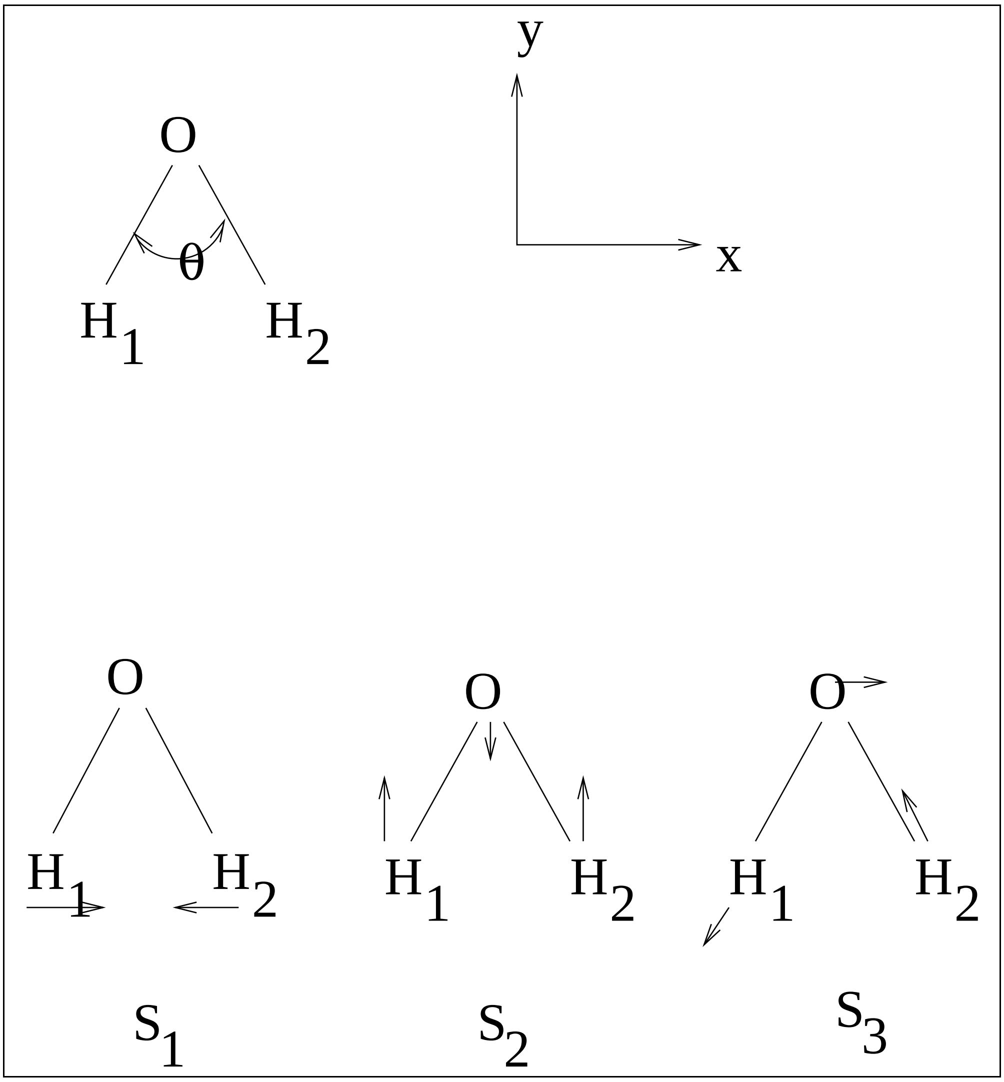

FIG. 2: Symmetry Coördinates for Water

$$\dot{y}_O^2 = \left(\frac{2m_H\dot{S}_2}{m_O}\right)^2$$

and finally,

$$\dot{x}_{H_2} = -\dot{S}_1 - \dot{S}_3 \sin\frac{\theta}{2} \tag{9}$$

$$\dot{y}_{H_2} = \dot{S}_2 + \dot{S}_3 \cos\frac{\theta}{2} \tag{10}$$

and squaring and finally adding appropriately one obtains

$$\dot{x}_{H_2}^2 = +\dot{S}_1^2 + 2\dot{S}_1\dot{S}_3 \sin\frac{\theta}{2} + \left(\dot{S}_3\frac{\theta}{2}\right)^2$$

$$\dot{y}_{H_2}^2 = \dot{S}_2^2 + 2\dot{S}_2\dot{S}_3 \cos\frac{\theta}{2} + \left(\dot{S}_3 \cos\frac{\theta}{2}\right)^2$$

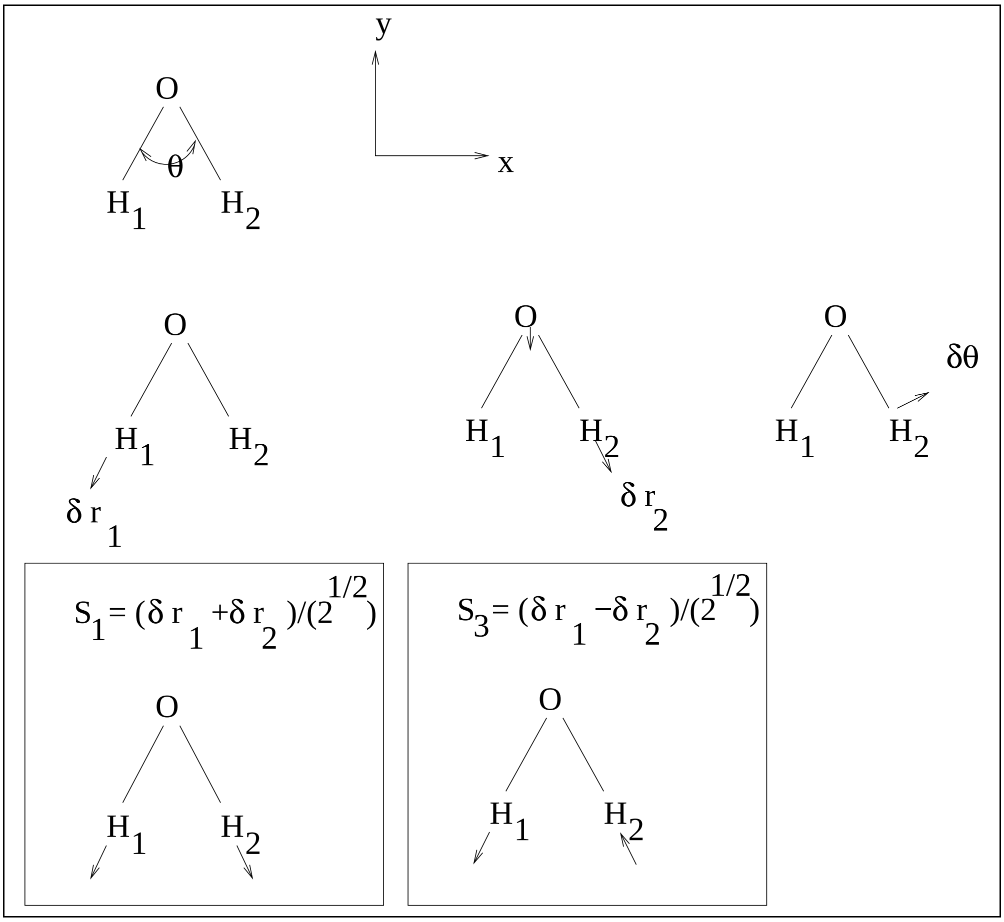

FIG. 3: Symmetry Coördinates for Water

Adding these three

$$m_H\left(\dot{x}_{H_1}^2+\dot{y}_{H_1}^2+\dot{x}_{H_2}^2+\dot{y}_{H_2}^2\right)+m_O\left(\dot{x}_O^2+\dot{y}_O^2+\right)=$$
$$m_H\left(2\dot{S}_1^2+2\dot{S}_2^2+2\dot{S}_3^2\right)+m_O\left(\left(\frac{2m_H}{m_O}\right)^2\left(\dot{S}_3^2\sin^2\frac{\theta}{2}+\dot{S}_2^2\right)\right)$$

so

$$T=\frac{1}{2}\left(m_H\left(2\dot{S}_1^2+2\dot{S}_2^2+2\dot{S}_3^2\right)+m_O\left(\left(\frac{2m_H}{m_O}\right)^2\left(\dot{S}_3^2\sin^2\frac{\theta}{2}+\dot{S}_2^2\right)\right)\right) \tag{11}$$

$$T=m_H\left(\dot{S}_1^2+\dot{S}_2^2+\dot{S}_3^2\right)+2m_O\left(\left(\frac{m_H}{m_O}\right)^2\left(\dot{S}_3^2\sin^2\frac{\theta}{2}+\dot{S}_2^2\right)\right) \tag{12}$$
$$=m_H\dot{S}_1^2+m_H\left(1+2\frac{m_H}{m_O}\right)\dot{S}_2^2+m_H\left(1+2\frac{m_H}{m_O}\sin^2\frac{\theta}{2}\right)\dot{S}_3^2$$

Notice, there are no cross terms.

What is the relationship between the internal coördinates and these symmetry coördinates? We write the cartesian diplacement of the atoms thus

$$\Delta r_{O-H_1} = \Delta x_O \sin\frac{\theta}{2} - \Delta x_{H_1} \sin\frac{\theta}{2} + \Delta y_O \cos\frac{\theta}{2} - \Delta y_{H_1} \cos\frac{\theta}{2}$$

$$\Delta r_{O-H_1} = (\Delta x_O - \Delta x_{H_1}) \sin\frac{\theta}{2} + (\Delta y_O - \Delta y_{H_1}) \cos\frac{\theta}{2} \tag{13}$$

$$= (-a - c) \sin\frac{\theta}{2} + (b + d) \cos\frac{\theta}{2} \tag{14}$$

For simplicity, the two outer force constants are called k_1 and the inner

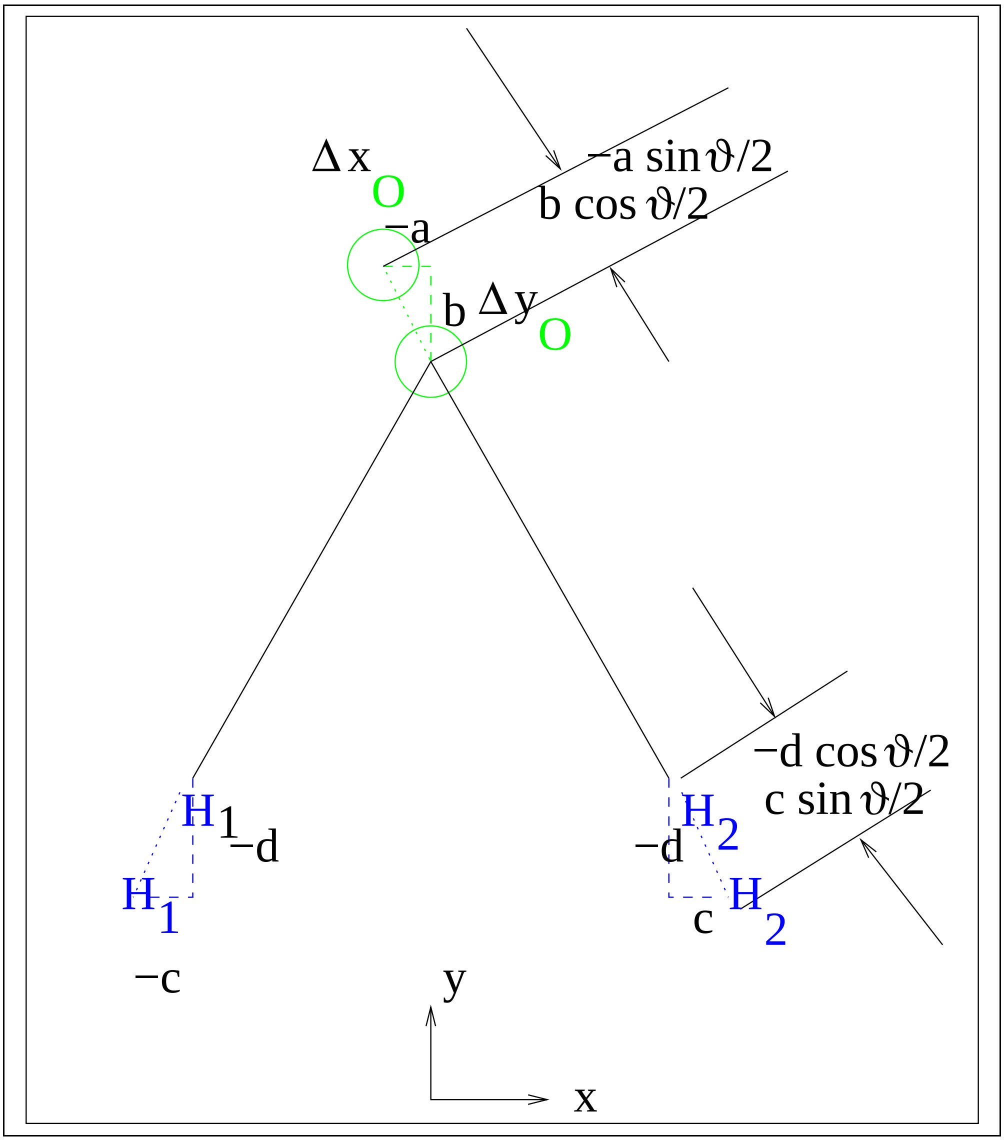

FIG. 4: Construction of internal displacement coordinates

$$\Delta r_{O-H_2} = -(\Delta x_O - \Delta x_{H_2}) \sin\frac{\theta}{2} + (\Delta y_O - \Delta y_{H_2}) \cos\frac{\theta}{2} \tag{15}$$

$$\Delta\theta = \frac{2}{r_{eq}}\left\{-\left(\Delta x_{H_2} - \Delta x_{H_1}\right)\cos\frac{\theta}{2} + \left(\Delta y_{H_2} + \Delta y_{H_1}\right)\sin\frac{\theta}{2} - 2\Delta y_O \sin\frac{\theta}{2}\right\} \tag{16}$$

so, substituting using Equations 7 and 5, we obtain

$$\begin{aligned}\Delta r_{O-H_1} &= \left(\frac{2m_H S_3 \frac{\theta}{2}}{m_O} - S_1 + S_3\frac{\theta}{2}\right)\sin\frac{\theta}{2} \\ &+ \left(\frac{2m_H}{m_O}S_2 - \left(S_2 - S_3\cos\frac{\theta}{2}\right)\right)\cos\frac{\theta}{2}\end{aligned} \tag{17}$$

$$\begin{aligned}\Delta r_{O-H_1} &= \frac{2m_H S_3 \sin^2\frac{\theta}{2}}{m_O} - S_1\sin\frac{\theta}{2} + S_3\sin^2\frac{\theta}{2} \\ &+ \frac{2m_H}{m_O}S_2\cos\frac{\theta}{2} - S_2\cos\frac{\theta}{2} + S_3\cos^2\frac{\theta}{2}\end{aligned} \tag{18}$$

$$\Delta r_{O-H_1} = -S_1\sin\frac{\theta}{2} + \left(\frac{2m_H}{m_O} - 1\right)S_2\cos\frac{\theta}{2} + S_3\left(1 + \frac{2m_H\sin^2\frac{\theta}{2}}{m_O}\right)$$

We also have

$$\begin{aligned}\Delta r_{O-H_2} &= -\left(\frac{2m_H S_3\sin\frac{\theta}{2}}{m_O} - (-S_1 - S_3\frac{\theta}{2})\right)\sin\frac{\theta}{2} \\ &+ \left(\frac{2m_H S_2}{m_O} - (S_2 + S_3\cos\frac{\theta}{2})\right)\cos\frac{\theta}{2}\end{aligned} \tag{19}$$

which is

$$\Delta r_{O-H_2} = -S_1\sin\frac{\theta}{2} + \left(\frac{2m_H}{m_O} - 1\right)S_2\cos\frac{\theta}{2} - S_3\left(\cos^2\frac{\theta}{2} + \sin^2\frac{\theta}{2} - \frac{2m_H\sin^2\frac{\theta}{2}}{m_O}\right) \tag{20}$$

i.e.,

$$\Delta r_{O-H_2} = -S_1\sin\frac{\theta}{2} + \left(\frac{2m_H}{m_O} - 1\right)S_2\cos\frac{\theta}{2} - S_3\left(1 - \frac{2m_H\sin^2\frac{\theta}{2}}{m_O}\right) \tag{21}$$

and finally,

$$\begin{aligned}\frac{r_{eq}}{2}\Delta\theta &= -\left(-S_1 - S_3\sin\frac{\theta}{2} - (S_1 - S_3\frac{\theta}{2})\right)\cos\frac{\theta}{2} \\ &+ \left((S_2 + S_3\cos\frac{\theta}{2}) + (S_2 - S_3\cos\frac{\theta}{2})\right)\sin\frac{\theta}{2} - 2\frac{2m_H S_2}{m_O}\sin\frac{\theta}{2}\end{aligned} \tag{22}$$

which simplifies to

$$2S_1\cos\frac{\theta}{2} + 2\left(1 - 2\frac{m_H}{m_O}\right)S_2\sin\frac{\theta}{2}$$

Substituting into Equation 4 we have

$$2V =$$

$$
\begin{aligned}
k_{O-H_1}(\delta r_{O-H_1})^2 &= k_{O-H_1}\left(-S_1\sin\frac{\theta}{2}+\left(\frac{2m_H}{m_O}-1\right)S_2\cos\frac{\theta}{2}+S_3\left(1+\frac{2m_H\sin^2\frac{\theta}{2}}{m_O}\right)\right)^2\\
+k_{O-H_2}(\delta r_{O-H_2})^2 &= k_{O-H_2}\left(-S_1\sin\frac{\theta}{2}+\left(\frac{2m_H}{m_O}-1\right)S_2\cos\frac{\theta}{2}-S_3\left(1-\frac{2m_H\sin^2\frac{\theta}{2}}{m_O}\right)\right)^2\\
+k_{H-O-H}(\delta\theta)^2 &= k_{H-O-H}\left(2S_1\cos\frac{\theta}{2}+2\left(1-2\frac{m_H}{m_O}\right)S_2\sin\frac{\theta}{2}\right)^2 \quad (23)
\end{aligned}
$$

$$
\begin{aligned}
2V &= \\
& k_{O-H}\left(-S_1\sin\frac{\theta}{2}+\left(\frac{2m_H}{m_O}-1\right)S_2\cos\frac{\theta}{2}+S_3\left(1+\frac{2m_H\sin^2\frac{\theta}{2}}{m_O}\right)\right)^2\\
& k_{O-H}\left(-S_1\sin\frac{\theta}{2}+\left(\frac{2m_H}{m_O}-1\right)S_2\cos\frac{\theta}{2}-S_3\left(1-\frac{2m_H\sin^2\frac{\theta}{2}}{m_O}\right)\right)^2\\
& k_{H-O-H}\left(2S_1\cos\frac{\theta}{2}+2\left(1-2\frac{m_H}{m_O}\right)S_2\sin\frac{\theta}{2}\right)^2 \quad (24)
\end{aligned}
$$