In which we count degrees of freedom and find the normal modes of a mess o’ masses and springs, which is a lovely model of a solid.

Two pendulums coupled with a spring may oscillate at the same frequency in two ways: the “parallel play” mode, in which the two pendulums move back and forth maintaining a constant distance between them, and the love-hate mode, in which they move in opposition. This latter mode oscillates at higher frequency, because the restoring torque caused by the spring augments the gravitational restoring torque, thus providing a greater incentive for each pendulum to return to equilibrium.

For an arbitrary initial condition, both modes will be stimulated and the motion will not be periodic (unless the frequencies happen to be commensurate). We call the simple case in which all masses in a system oscillate at the same frequency a normal mode of oscillation.

Suppose that the pendulums have length $\ell$, mass $m$, and are linked at their midpoints by a spring of spring constant $k$. Taking the zero of potential energy at the point of suspension of the pendulums, the lagrangian of this system is approximately

$$L = \frac{1}{2} m\ell^2 (\dot{\theta}_1^2 + \dot{\theta}_2^2) + mg\ell (\cos \theta_1 + \cos \theta_2) - \frac{1}{2} k \left( \frac{\ell}{2} \right)^2 (\theta_1 - \theta_2)^2$$

where I have neglected the vertical displacement of the ends of the springs and approximated their horizontal displacement as $\ell \theta/2$. In fact, in this approximation, the cosine terms may be simplified to their lowest nontrivial dependence on each angle, giving (up to a constant)

$$L = \frac{1}{2} m\ell^2 (\dot{\theta}_1^2 + \dot{\theta}_2^2) - \frac{mg\ell}{2} (\theta_1^2 + \theta_2^2) - \frac{1}{2} k \left( \frac{\ell}{2} \right)^2 (\theta_1 - \theta_2)^2$$

The Lagrange equations for this system are therefore

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\theta}_1} \right) - \frac{\partial L}{\partial \theta_1} = m\ell^2 \ddot{\theta}_1 + mg\ell \dot{\theta}_1 + \frac{k\ell^2}{4} (\theta_1 - \theta_2) = 0$$

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\theta}_2} \right) - \frac{\partial L}{\partial \theta_2} = m\ell^2 \ddot{\theta}_2 + mg\ell \dot{\theta}_2 + \frac{k\ell^2}{4} (\theta_2 - \theta_1) = 0$$
Divide these equations by $m\ell^2$ to tidy them up a bit:

\begin{align*}
\ddot{\theta}_1 + \frac{g}{\ell} \theta_1 + \frac{k}{4m} (\theta_1 - \theta_2) &= 0 \\
\ddot{\theta}_2 + \frac{g}{\ell} \theta_2 + \frac{k}{4m} (\theta_2 - \theta_1) &= 0
\end{align*}

What happens to these equations if $\theta_1(t) = \theta_2(t)$? Then the coupling terms disappear and we are left with identical simple harmonic oscillator equations. So, we deduce that one solution is of the form

$$\theta_1 = \theta_2 = c_1 \cos(\omega_0 t + \phi_1) = d_1 \cos \omega_0 t + d_2 \sin \omega_0 t$$

(7)

where $\omega_0^2 = g/\ell$, and $c_1$ and $\phi_1$ (or equivalently $d_1$ and $d_2$) are constants to be determined by initial conditions.

A second solution may be found by assuming that $\theta_1 = -\theta_2$. Then the first equation becomes

$$\ddot{\theta}_1 + \frac{g}{\ell} \theta_1 + \frac{k}{2m} \theta_1 = 0$$

which is also the simple harmonic oscillator equation, with solution

$$\theta_1 = -\theta_2 = c_2 \cos(\omega_1 t + \phi_2)$$

(8)

where $\omega_1 = \sqrt{\frac{g}{\ell} + \frac{k}{2m}}$, and $c_2$ and $\phi_2$ are constants.

The two boxed equations are the two normal modes of the coupled pendulum system. In a normal mode, all the particles oscillate at the same frequency (but not necessarily the same amplitude or phase). An arbitrary motion of the unforced system is a linear combination (superposition) of the two normal modes, with amplitudes and phases chosen to match the given initial conditions.

**Example 1** At $t = 0$ we thump the first mass. What is the subsequent motion?

We’ll assume that the thump takes place over negligible time, and serves to launch $m_1$ at some initial angular velocity $\dot{\theta}_1(0) = \Omega$. If the first normal mode is described by $d_1 \cos \omega_0 t + d_2 \sin \omega_0 t$, while the second is described
by $d_3 \cos \omega_1 t + d_4 \sin \omega_1 t$, then
\[
\begin{align*}
\theta_1(0) &= d_1 + d_3 & \dot{\theta}_1(0) &= d_2 \omega_0 + d_4 \omega_1 = \Omega \\
\theta_2(0) &= d_1 - d_3 & \dot{\theta}_2(0) &= d_2 \omega_0 - d_4 \omega_1 = 0
\end{align*}
\]

The angular positions require that $d_1 = d_3 = 0$, while the angular velocities require that $d_2 \omega_0 = d_4 \omega_1 = \Omega/2$. Therefore,
\[
\begin{align*}
\theta_1(t) &= \frac{\Omega}{2\omega_0} \sin \omega_0 t + \frac{\Omega}{2\omega_1} \sin \omega_1 t \\
\theta_2(t) &= \frac{\Omega}{2\omega_0} \sin \omega_0 t - \frac{\Omega}{2\omega_1} \sin \omega_1 t
\end{align*}
\] (9) (10)

For weak coupling, $\omega_1$ is not much greater than $\omega_0$, so the two terms beat at a frequency given by the difference between $\omega_1$ and $\omega_0$; the energy is gradually traded from one oscillator to the other and back, as illustrated below.

In the language of linear algebra, a normal mode could be described as a column vector, with the amplitude and phase of motion of each variable an element of the vector. The two eigenvectors of the example could be notated
\[
\begin{align*}
a_+ &= \frac{1}{\sqrt{2}} \left( \begin{array}{c} 1 \\ 1 \end{array} \right) & \text{and} & a_- &= \frac{1}{\sqrt{2}} \left( \begin{array}{c} 1 \\ -1 \end{array} \right)
\end{align*}
\]

so that the general solution might be expressed
\[
\begin{pmatrix} \theta_1(t) \\ \theta_2(t) \end{pmatrix} = \text{Re} \left[ A_+ e^{-i \omega_1 t} a_+ + A_- e^{-i \omega_0 t} a_- \right]
\]

for (complex) amplitudes $A_+$ and $A_-$. 

1. Generalization to N Coupled Particles

We now wish to generalize this example to a system of \( N \) masses coupled with various springs to form a molecule or solid with a stable equilibrium configuration. On perturbing one or more of the masses from equilibrium, what sort of motion arises?

The motion is bound to be complicated, with each mass ending up coupled to every other one via the intermediary of one or more springs. It seems reasonable that even if all masses were initially at rest, they will all end up moving in some complicated fashion. **The amazing result, however, is that we can always decompose the motion into a linear combination of vibrations in normal modes, with each particle vibrating at the same frequency.** Typically, the normal modes oscillate at different frequencies, however, so their superposition produces a motion significantly more complicated than sinusoidal. The motion within each normal mode takes place independent of that in every other; each normal mode vibration is described with a single amplitude and phase. Hence, the complete behavior is specified by determining the amplitude and phase of vibration in each of the normal modes.

If the system is three-dimensional, we will need \( 3N \) generalized coordinates \( q_j \) \((j = 1, 2, \ldots, 3N)\) to describe the configuration of the system, and a corresponding number of generalized velocities \( \dot{q}_j \). Of the \( 3N \) degrees of freedom, 3 correspond to the center of mass translation of the system, and 3 to its rotation (unless the system happens to be a linear molecule, in which case the molecule can rotate only about two axes). None of these coordinates has a restoring force; absent external influences, their momenta will be constants of the motion. I think that it’s easiest to think of these modes as a special sort of normal mode with vanishing frequency.

This leaves \( 3N - 6 \) degrees of freedom associated with distortions away from equilibrium positions (except for linear molecules, in which case there are \( 3N - 5 \) remaining degrees of freedom associated with normal modes of nonzero frequency). We will show that each of these gives rise to a **normal mode** of vibration, in which all the masses oscillate at the same (nonzero) frequency. Furthermore, each normal mode is independent of all the others, so that the \( 3N - 6 \) coupled oscillators factor into \( 3N - 6 \) decoupled (independent) oscillators.

We will work in the center of mass frame and disregard rigid-body rotation. Then in the equilibrium configuration,

\[
q_j = q_{j0}, \quad \dot{q}_j = 0, \quad \ddot{q}_j = 0, \quad j = 1, 2, \ldots, n
\]

where \( n = 3N - 6 \) (or \( 3N - 5 \) if linear). Lagrange’s equation for the \( j \)th coordinate

**We will consider rigid-body rotations and center-of-mass translations as normal modes of vanishing frequency.**

**In the limit we consider, where the potential is strictly a quadratic function of the coordinates, each normal mode is independent of every other one, and the full motion is a linear superposition of the motion of each normal mode.**
1. Generalization to \( N \) Coupled Particles

is,

\[
\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_j} \right) - \frac{\partial L}{\partial q_j} = 0
\]

The first term must contain either \( \dot{q}_j \) or \( \ddot{q}_j \), both of which vanish. Therefore, \( \frac{\partial L}{\partial \dot{q}_j} = \frac{\partial U}{\partial q_j} = 0 \). With no loss of generality, we may shift the origin of each generalized coordinate to \( q_{j0} \). Then expanding the potential about the equilibrium position in a Taylor series through second order, we have

\[
U(q_1, q_2, \ldots, q_n) = U_0 + \sum_j \frac{\partial U}{\partial q_j} \bigg|_{q_{j0}} q_j + \frac{1}{2} \sum_{j,k} \frac{\partial^2 U}{\partial q_j \partial q_k} \bigg|_{q_{j0}} q_j q_k + \cdots
\]

\[
\approx U_0 + \frac{1}{2} A_{jk} \dot{q}_j \dot{q}_k \tag{11}
\]

where we use the summation convention in the final expression (and henceforth). The linear term vanishes in equilibrium because we are at a potential minimum. Equation (11) defines the spring matrix,

\[
A_{jk} = \left. \frac{\partial^2 U}{\partial q_j \partial q_k} \right|_0 \tag{12}
\]

which characterizes the stiffness of the bonds that hold each particle in its equilibrium position.

Apart from the constant term in front, Eq. (11) says that for small displacements from equilibrium the potential energy increases quadratically with the displacement, no matter in which combination of generalized coordinates we make the displacement. Furthermore, if the equations of transformation are not explicit functions of the time, then the kinetic energy is a homogeneous quadratic function of the generalized velocities\[1\]

\[
T = \frac{1}{2} m_{jk} \dot{q}_j \dot{q}_k \tag{15}
\]

\[1\]If the system comprises \( N \) particles whose Cartesian coordinates are \( x_{a,i} \), with \( a = 1, 2, \ldots, N \) and \( i = 1, 2, 3 \) indexing the component of the Cartesian position vector of the \( a \)th particle, then

\[
T = \sum_{a=1}^{N} \sum_{i=1}^{3} \frac{1}{2} m_{a} x_{a,i}^2 \tag{13}
\]

Expressing the positions in terms of generalized coordinates, and assuming that the equations of transformation are not explicit functions of time, we have

\[
T = \sum_{a=1}^{N} \frac{1}{2} m_{a} \left( \frac{\partial x_{a,i}}{\partial q_j} \right) \left( \frac{\partial x_{a,i}}{\partial q_k} \right) \dot{q}_j \dot{q}_k = \frac{1}{2} \sum_{j,k} m_{jk} \dot{q}_j \dot{q}_k \tag{14}
\]

where \( m_{jk} = \sum_{a} m_{a} \frac{\partial x_{a,i}}{\partial q_j} \frac{\partial x_{a,i}}{\partial q_k} \), and a sum over Cartesian index \( i \) is implied.
1. Generalization to N Coupled Particles

where $m_{jk}$ is the **mass matrix**.

Therefore, if all the displacements from equilibrium are small enough that the quadratic approximation to the potential is valid, the lagrangian of the system is expressible in terms of two symmetric $n \times n$ matrices, the mass matrix $m_{jk}$ and the spring matrix $A_{jk}$, as

$$L = T - U = \frac{1}{2} m_{jk} \dot{q}_j \dot{q}_k - \frac{1}{2} A_{jk} q_j q_k$$

(16)

Lagrange’s equations are thus

$$A_{jk} q_j + m_{jk} \ddot{q}_j = 0$$

(17)

This is a set of $n$ coupled second-order differential equations, since $k = 1, 2, \ldots, n$ and we are implicitly summing over the repeated index $j$.

To solve Eq. (17), we use our experience with oscillatory systems and guess that we can find solutions that oscillate sinusoidally in time. We will hope that we can find solutions in which every particle oscillates at the same frequency. So, we guess $q_j = a_j e^{-i \omega t}$, which allows us to convert the coupled second-order differential equations into coupled linear equations in the square of the angular frequency $\omega$:

$$(A_{jk} - \omega^2 m_{jk}) a_j = 0 \quad \text{or} \quad (A - \omega^2 M) a = 0$$

(18)

where the second form is written as an explicit matrix equation. For a nontrivial solution, the determinant $|A - \omega^2 M|$ must vanish, which is an $n$th order equation for $\omega^2$ called the **characteristic equation** or the **secular equation**. It therefore has $n$ roots (some of which may be degenerate). Because $A$ and $M$ are real, symmetric matrices, and because both $T$ and $U$ are non-negative, it is possible to show that

1. all the eigenvalues $\omega^2$ are real and positive;

2. the eigenvectors $a_r$ are orthogonal, and can be normalized to yield an orthonormal basis, $a_r = a_r j e_j$; and

3. the configuration of the system may be expressed in terms of the normalized eigenvectors using **normal coordinates**, $\eta_r$, which satisfy $\ddot{\eta}_r + \omega_r^2 \eta_r = 0$, where $\omega_r$ is the corresponding eigenfrequency, $q_j(t) = \text{Re} \left( \sum_r a_{jr} \eta_r e^{-i \omega_r t} \right)$.

An eigenvector (or normal mode vector) specifies the amplitude and phase of vibration of each coordinate $q_j$. The unit vectors $e_j$ point in the direction of increasing $q_j$.

Thus, the complicated system of $3N$ degrees of freedom reduces to $3N - 6$ normal modes in each of which all masses oscillate at the same frequency, 3 degrees of freedom (modes) for the center-of-mass translation, and 3 degrees of freedom (modes) for rigid-body rotation.
2. Linear Algebra

Perhaps you are so familiar with linear algebra that the above consequences are obvious. If so, you had a much better course than I did (which, frankly, isn't saying much!). You can skip to the example.

In the following I will omit the summation signs and use the Einstein summation convention, so that Eq. (11) is

\[ U - U_0 = \frac{1}{2} A_{jk} q_j q_k \geq 0 \]  

and Eq. (18) is

\[ (A_{jk} - \omega^2 m_{jk}) a_k = 0 \]

2.1 Normal-mode frequencies are real

We would like to show that \( \omega^2 \) is real and positive, as we fully expect on physical grounds. Multiply by the complex conjugate of \( a_j \) and sum over \( j \):

\[ A_{jk} a_j^* a_k = \omega^2 m_{jk} a_j^* a_k \implies \omega^2 = \frac{A_{jk} a_j^* a_k}{m_{jk} a_j^* a_k} \]

Both the numerator and denominator have the same form, which we would like to show is both real and positive. To show that the numerator is real, take its complex conjugate:

\[ (A_{jk} a_j^* a_k)^* = A_{jk}^* a_j a_k^* = A_{kj} a_j a_k^* = (A_{kj} a_j a_k)^* \]

A \( j \) and \( k \) are related.

Hence, \( \omega^2 \) is real and positive definite, so the eigenfrequencies are positive definite, also.

Remember, the components \( a_k \) of the eigenvector \( a \) specify the amplitude and phase of motion of generalized coordinate \( q_k \).
2.2 The Eigenvectors are orthogonal

To show that the eigenvectors are orthogonal, assume that we have two distinct eigenfrequencies, \( \omega_r \) and \( \omega_s \):

\[
\begin{align*}
(A_{jk} - \omega_s^2 m_{jk}) a_{ks} &= 0 \\
(A_{kj} - \omega_r^2 m_{kj}) a_{jr} &= 0
\end{align*}
\]

Because both \( A_{jk} \) and \( m_{jk} \) are symmetric, I can rewrite the second equation as

\[
(A_{jk} - \omega_r^2 m_{jk}) a_{jr} = 0
\]

Now multiply the first equation by \( a_{jr} \) and sum, multiply the second by \( a_{ks} \) and sum, and subtract the results to get

\[
(\omega_r^2 - \omega_s^2) m_{jk} a_{jr} a_{ks} = 0 \quad (20)
\]

When \( \omega_s \neq \omega_r \), this implies that

\[
m_{jk} a_{jr} a_{ks} = 0 \quad (\omega_r \neq \omega_s) \quad (21)
\]

which is the orthogonality condition. If \( \omega_r = \omega_s \), then we can't tell about \( m_{jk} a_{jr} a_{ks} \) from Eq. (20). If \( r = s \), however, it is a quadratic form, which we have shown must be positive definite. We are free to normalize the eigenvector so that it has unit length. When there are multiple modes with the same frequency, it is always possible to diagonalize this subspace to produce orthogonal eigenvectors. Hence, the normalized eigenvectors satisfy

\[
m_{jk} a_{jr} a_{ks} = \delta_{rs} \quad (22)
\]

where \( \delta_{rs} \) is the Kronecker delta.

**Example 2**  Find the vibration frequencies and normal modes of CO\(_2\).

Let the mass of the central carbon atom be \( M \), the mass of the oxygen atoms be \( m \), and the spring constant of the C–O bond be \( k \). Align the molecule with the \( x \) axis and assume it is not rotating. Working in the
center of mass frame, we have

$$\sum_{i=1}^{3} m_i r_i = 0 = m(r_1 + r_3) + Mr_2$$  \hspace{1cm} (23)$$

Since we are working in the center of mass frame, there are two possibilities: either the atoms vibrate along the axis that joins their centers (the springs are stretched and compressed), or they move perpendicular to that axis. The former is called a **longitudinal vibration**, while the latter is a **transverse vibration**. For a mode with nonzero vibration frequency, the angular momentum must vanish, so transverse modes will involve bending of the molecule.

**Longitudinal Vibrations**

Consider first a motion purely along the axis of the molecule. We should anticipate a mode in which the carbon stays put and the two oxygens oscillate out of phase with one another. This mode should have the frequency $\sqrt{k/m}$, since it is as though the oxygen atom is bound by a spring to a fixed wall.

The other mode should involve the oxygen atoms heading left when the carbon heads right, and should be at higher frequency, because both springs work to restore the carbon to its equilibrium position.

$$m(x_1 + x_3) = -Mx_2 \implies x_2 = -\mu(x_1 + x_3)$$

where $\mu \equiv m/M$. so that we may write the kinetic energy

$$T = \frac{m}{2}(\dot{x}_1^2 + \dot{x}_3^2) + \frac{M}{2} \dot{x}_2^2 = \frac{m}{2} \left[(1 + \mu)(\dot{x}_1^2 + \dot{x}_3^2) + 2\mu \dot{x}_1 \dot{x}_3\right]$$

Hence,

$$m_{jk} = \begin{pmatrix} 1 + \mu & \mu \\ \mu & 1 + \mu \end{pmatrix}$$

Notice that we have to divide the cross term equally between $m_{12}$ and $m_{21}$, since $m_{ij}$ is a symmetric matrix. Similarly, the potential energy is

$$U - U_0 = \frac{k}{2} \left[(x_2 - x_1)^2 + (x_3 - x_2)^2\right] = \frac{k}{2} \left[(2\mu^2 + 2\mu + 1)(\dot{x}_1^2 + \dot{x}_3^2) + 4\mu(\mu + 1)x_1x_3\right]$$

so

$$A_{jk} = \begin{pmatrix} 2\mu^2 + 2\mu + 1 & 2\mu(\mu + 1) \\ 2\mu(\mu + 1) & 2\mu^2 + 2\mu + 1 \end{pmatrix}$$
The characteristic equation is \((A_{jk} - \omega^2 m_{jk})a_k = 0\), so that for a nontrivial solution we must have
\[
\begin{vmatrix} k(2\mu^2 + 2\mu + 1) - m(1 + \mu)\omega^2 & 2\mu(\mu + 1) - m\mu\omega^2 \\ 2k\mu(\mu + 1) - m\mu\omega^2 & k(2\mu^2 + 2\mu + 1) - m(1 + \mu)\omega^2 \end{vmatrix} = 0 \tag{24}
\]
which means that
\[
k(2\mu^2 + 2\mu + 1) - m(1 + \mu)\omega^2 = \pm \left[ 2\mu(\mu + 1) - m\mu\omega^2 \right] \\
k[1 + \mu(\mu + 1)(2 + 2)] = m\omega^2(1 + \mu) \\
\omega^2 = \frac{k}{m} \frac{1 + (2 + 2)\mu(\mu + 1)}{1 + \mu + \mu}
\]
Thus, the two frequencies are
\[
\omega_- = \sqrt{\frac{k}{m}} \quad \text{and} \quad \omega_+ = \sqrt{\frac{k}{m} \sqrt{1 + 2\mu}}
\]
Before substituting the eigenvalues back into the determinant to find the eigenvectors (normal mode displacement amplitudes), let’s pull out a common factor of \(k/m\) to get
\[
\begin{vmatrix} 2\mu^2 + 2\mu + 1 - m\omega^2/k & 2\mu(\mu + 1) - m\mu\omega^2/k \\ 2\mu(\mu + 1) - m\mu\omega^2/k & 2\mu^2 + 2\mu + 1 - m\omega^2/k \end{vmatrix} = 0 \tag{25}
\]
Substituting \(\omega_-\) into the secular determinant to solve for the eigenvector, we get
\[
2k\mu(\mu + 1) \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} a_{-1} \\ a_{-3} \end{pmatrix} = 0 \quad \Rightarrow \quad a_- = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}
\]
Sure enough, in this mode the displacements of the two oxygen atoms are equal and opposite.
Substituting \(\omega_+\) into the secular determinant to solve for the eigenvector, we get
\[
\begin{vmatrix} -1 & 1 \\ 1 & -1 \end{vmatrix} \begin{pmatrix} a_{-1} \\ a_{-3} \end{pmatrix} = 0 \quad \Rightarrow \quad a_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}
\]
We may readily confirm that these eigenvectors are orthogonal:
\[
\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} m \begin{pmatrix} 1 + \mu & \mu \\ \mu & 1 + \mu \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = 0
\]
It is worth noting that the orthogonality condition is a bit more complicated than a simple dot product between the eigenvectors, but requires the intervention of the mass matrix.
Transverse Vibrations

For motion perpendicular to the molecular axis, the zero-rotation condition requires that \( y_1 = y_3 \) and since \( m(y_1 + y_3) + M y_2 = 0 \), that \( y_2 = -\frac{2m}{M} y_1 = -2\mu y_1 \). The kinetic energy is

\[
T = \frac{m}{2} \left[ 2\dot{y}_1^2 + \mu^{-1} \dot{y}_2^2 \right] = \frac{m}{2} \left[ 2\dot{y}_1^2 + 4\mu \dot{y}_1^2 \right] = m\dot{y}_1^2(1 + 2\mu)
\]

Using the Pythagorean theorem, we can compute the stretch of the springs as

\[
\xi = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 - (x_2 - x_1)}.
\]

Let \( \ell = x_2 - x_1 \) be the bond length. Then

\[
U = 2\frac{k}{2} \left[ \ell^2 + y_1^2(1 + 2\mu)^2 + \ell^2 - 2\ell \sqrt{\ell^2 + y_1^2(1 + 2\mu)^2} \right]
\]

\[
= 2k\ell^2 \left[ 1 + \frac{y_1^2(1 + 2\mu)^2}{2\ell^2} - \sqrt{1 + \frac{y_1^2(1 + 2\mu)^2}{\ell^2}} \right]
\]

\[
\approx 0 + O(y_1^4)
\]

where I have used the binomial approximation to simplify the radical. That is, if we just consider the stretch of the spring, we get nothing until order \( y_1^4 \). That's not too promising.

If we consider, instead, that the molecule likes to be straight and that it experiences a restoring torque proportional to the bending angle, then

\[
U \propto \left( \frac{y_1 - y_2}{\ell} \right)^2 = \left( \frac{y_1(2\mu + 1)}{\ell} \right)^2
\]

where \( \ell \) is the bond length. Let us suppose that the constant of proportionality is

\[
U = 2 \times \frac{1}{2} k(y^2 \ell^2) \left[ \frac{y_1(2\mu + 1)}{\ell} \right]^2 = k\gamma^2[y_1(2\mu + 1)]^2
\]  

(26)

where \( \gamma \) is a dimensionless constant that compares the bending stiffness to the stretching stiffness of the bond. The energy of the molecule in this mode is thus

\[
E = T + U = m\dot{y}_1^2(1 + 2\mu) + k\gamma^2(2\mu + 1)^2 y_1^2
\]

Taking the ratio of the coefficient of the \( y_1^2 \) term to the \( \dot{y}_1^2 \) term gives the square of the transverse vibration frequency,

\[
\omega_T^2 = \frac{k\gamma^2(1 + 2\mu)^2}{m(1 + 2\mu)} \implies \omega_T = \gamma \sqrt{\frac{k}{m} \sqrt{1 + 2\mu}}
\]
Now it is time to touch base with reality. The observed vibration frequencies of carbon dioxide are 667 : 1288 : 2349 (cm$^{-1}$). Note that I have quoted the vibration frequencies in the unit chemists and molecular spectroscopists seem to prefer: wave numbers. These correspond to wavelengths 14.99, 7.76, and 4.26 µm, in the spectral region of the thermal (re)radiation from the Earth.

The absorption bands of atmospheric gases are shown in the figure (next page). Carbon dioxide absorbs strongly near 15 µm and also near 4.5 µm. Only two of the three vibrational modes are “optically active,” meaning that they have a time-changing electric dipole moment and therefore couple strongly to electromagnetic radiation. When a light wave with the same frequency passes over the molecule, the electric field in the wave pushes positive and negative charges in opposite directions. Since oxygen is more electronegative than carbon, the carbon atom is slightly positively charged and the oxygen atoms slightly negatively charged. To a good approximation, the charge centers follow their respective nuclei as the molecule vibrates, and so the modes with nonzero dipole moment couple strongly to the electromagnetic field in the neighborhood of their resonant frequency. These are the transverse mode and the higher-frequency longitudinal mode. Evidently, therefore, we must associate the mode at 7.76 µm with the optically inert longitudinal mode of frequency $\frac{\gamma k}{m}$, which implies that the high-frequency mode should be at

$$\lambda = 7.76 \mu m \left(1 + \frac{16}{12}\right)^{-1/2} = 4.05 \mu m$$

which is pretty close to the observed value of 4.26 nm. The mode at lowest frequency, $\lambda = 14.99 \mu m$, is associated with the transverse (bending) vibration, from which we infer $\gamma \approx 667/2349 = 0.284$. That is, the spring is significantly softer in bending than in stretching, which seems perfectly reasonable.
2. **LINEAR ALGEBRA**

2.2 **The Eigenvectors are orthogonal**

**Summary**

Particles in an object that holds its shape are subject to restoring forces that restrict their motion to small excursions about their equilibrium positions. Expanding the potential about the equilibrium position to quadratic order leads to a set of coupled linear, second-order differential equations for the $3N$ generalized coordinates required to specify the configuration of the $N$ particles. Solutions may be found in which all particles oscillate with the same frequency; they are called normal modes. We will adopt the view that the zero-frequency modes (translations and rigid-body rotations) may also be termed “normal modes,” which simplifies the accounting. In total, therefore, there are $3N$ normal modes for a solid object of $3N$ particles. An arbitrary motion of the system (within the quadratic approximation for the potential) may be expressed as a superposition of the $3N$ normal modes by appropriate amplitudes and phases to match the initial conditions.