# Phys 326 Discussion 3 – Molecular Vibrations

One application of normal mode analysis is to describe the vibrational modes of molecules. Each vibrational mode has a characteristic frequency (usually in the infrared range for molecules) that can be seen by studying the molecule with spectroscopic techniques (e.g. by looking for absorption lines in an IR spectrum). A molecule's characteristic frequencies are its fingerprints, allowing it to be identified in a sample.

The figure at right is a classical model of the CO_2 molecule. The positively-charged carbon ion C^{++} is in the middle and has mass m, while the two negatively-charged oxygen ions O^- are on either side, each with mass M. The CO_2 molecule has no electric dipole moment, indicating that the ions lie on a line. (This is unlike the H_2O molecule, where the three ions form a triangle and a large electric dipole moment is present.) The springs provide a classical approximation to the covalent bonds between the atoms; we label their spring constants "k" as usual.
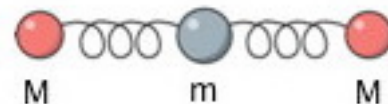
Problem 1 : Carbon Dioxide Longitudinal Motion   *Checkpoints* [1]

Let's define the $+x$ direction to be to the right, and restrict our attention to the case when the masses can move only in the x direction. Label the positions of the three atoms as usual: with x_1, x_2, and x_3, where $x_1 = x_2 = x_3 = 0$ puts the system in equilibrium (both springs unstretched).

(a) Use your small-oscillation skills to calculate the three eigenfrequencies and associated eigenvectors of this system. Don't fear the 3x3 determinant, it factors very nicely. :-)

(b) Hopefully you found a slow mode, a fast mode, and a "DC" mode of zero frequency. First consider the two non-zero frequencies: find the normal mode solutions $\vec{x}_s(t)$ for the slow mode and $\vec{x}_f(t)$ for the fast mode.

(c) In the language of molecular spectroscopy, the two modes you just found are called "symmetric stretch" and "asymmetric stretch" modes. Sketch the modes, then figure out which term is appropriate for the slow mode and which for the fast mode.

(d) To complete our solution, we must also write down the zero-frequency "DC mode", $\vec{x}_z(t)$. Think back to our discussion of DC modes in yesterday's lecture ... and remember that each mode must have <u>two</u> free parameters.

(e) Describe the molecule's motion in DC mode. Spectroscopists do not have a cute name for this mode … in fact they do not care about this mode (except to toss it away) … if you are unclear on why this is, ask your TA!

---

[1] (a) $\omega^2_{z,s,f} = 0, \dfrac{k}{M}, \dfrac{k}{M}\left(1 + \dfrac{2M}{m}\right)$ with corresponding eigenvectors $\vec{A}_{z,s,f} = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}, \begin{pmatrix} m \\ -2M \\ m \end{pmatrix}$

(b) $\vec{x}_{s,f}(t) = \vec{A}_{s,f}\cos(\omega_{s,f}t - \delta_{s,f})$ (c) slow mode = symmetric stretch, fast mode = asymmetric stretch

(d) Hint / reminder: go back to the equations of motion, $M\ddot{\vec{x}} = K\vec{x}$, and try solving $M\ddot{\vec{x}} = K\vec{x} = 0$. Answ: $\vec{x}_z(t) = \vec{A}_z(x_0 + v_0 t)$.

(f) Hint: the general SHO expression $A\cos(\omega t - \delta)$ can always be replaced with the equivalent form $B\cos(\omega t) + C\sin(\omega t)$, where we have traded the two free parameters A & δ for the alternate pair B & C. The <u>second</u> of these forms is usually much better for handling <u>initial conditions</u>! Answ: $x_1(t) = P_0\left[\dfrac{t}{m+2M} + \dfrac{\sin(\omega_s t)}{2M\omega_s} + \dfrac{m\sin(\omega_f t)}{2M(m+2M)\omega_f}\right]$

(f) Let's see how these modes combine to give us a general solution that can accommodate any initial conditions. Suppose our CO_2 molecule is sitting at rest and in equilibrium, with no atom moving … then, at time $t = 0$, an <u>impulse</u> P_0 in the $+x$ direction is delivered to the <u>left-hand</u> mass. (Whack!) Find the subsequent motion $x_1(t)$ of the left-hand mass. If you end up facing a great deal of algebra involving trig identities, an important hint is provided in the checkpoint.

Problem 2 : Springs on a Circle   *Checkpoints [2]*

Two masses m are constrained to move on a circular hoop. Identical springs of spring constant k are wrapped around the hoop and connect the masses to each other as shown. The hoop is placed horizontal to the ground so that gravity can be ignored. Finally, m and k are related by **$m = 2k$**.

The figure defines the equilibrium positions of the masses: at the top and at the bottom. Let x_1 & x_2 be the distances that the top & bottom masses are displaced from these equilibrium positions, measured <u>around the hoop</u> in the <u>clockwise</u> direction.

$m=2k$

k k

$m=2k$
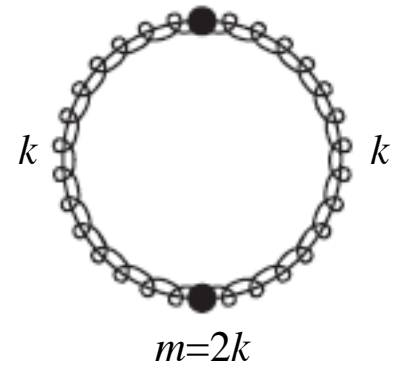
(a) Calculate the general small-oscillation solutions for $x_1(t)$ and $x_2(t)$.

(b) Describe the behaviour of the system's normal modes using words and/or sketches.

---

[2] (a) $\vec{x}(t) = \begin{pmatrix} 1 \\ 1 \end{pmatrix}(x_0 + v_0 t) + \begin{pmatrix} 1 \\ -1 \end{pmatrix} A \cos\left(\sqrt{2}t - \delta\right)$