1. **(Numerical Error Comparison)**

   Consider the following initial value problems:

   (i) $x' = x$, with $x(0) = 1$ on the interval $[0, 1]$, with $h_0 = 0.1$;

   (ii) $x' = x \sin 3t$, with $x(0) = 1$ on the interval $[0, 4]$, with $h_0 = 0.4$;

   (iii) $y' = y^2 \cos 2t$, with $y(0) = 1$ on the interval $[0, 6]$, with $h_0 = 0.5$.

   For each of these problems, carry out the following steps:

   a) Find the exact solution to the differential equation.

   b) For eight step sizes starting with h_0, and halving each time, that is $h_0, \frac{h_0}{2}, \frac{h_0}{2^2}, \ldots, \frac{h_0}{2^7}$, find the approximate solution using Euler's method. Make a figure that graphically compares the computed solutions with the exact solutions for different step sizes. (You can refer to Figure 2 in Section 6.1 of Polking's book.)

   c) Complete the tasks in b) for the Runge-Kutta methods of orders 2 and 4.

   d) Make a figure that graphically compares the computed solutions for each of the three methods at one of the step sizes with the exact solution. (You can refer to Figure 4 in Section 6.3 of Polking's book.)

   e) For each method and each step size, find and record the maximum error over the indicated interval. It would be best to record the maximum error by computer program, if possible. Plot the maximum errors in the three methods versus step size. If it is difficult or impossible to find the maximum error, then compute the error at the end of the computation interval.

   f) For each method, take the log of maximum errors in e), and the log of the step sizes, plot the log of maximum errors vs. the log of the step sizes (log-log plot). A figure like Figure 5 in Section 6.3 of Polking's book would be suitable. Observe that whether these plots look like straight lines. Approximate these plots by linear functions and compute the slopes. Do these slopes coincide with the order of accuracy of the method you use?

   g) Write a report to summarize all the above results and your findings.

2. (**Oscillations of Linear Molecules, Project 9.11 of Polking's Book**)

   Molecules are made up of atoms, which are bound together by bonding forces between the atoms. The atoms move within the molecule subject to these forces. In general the atomic bonds can stretch or compress, they can bend, or they can rotate. In addition molecules move through space under the influence of external forces, or, in the absence of external forces, in a purely inertial manner. For any particular molecule these motions can be modeled with a system of differential equations. As you can see, the combination of all of the motions can be quite complicated, and the resulting system of differential equations must be just as complicated.

   In this project we will examine the internal motion of linear molecules. These are molecules such as oxygen (O_2, see Figure 1), which has two atoms, and carbon dioxide (CO_2, see Figure 3), which has three. We will assume that there are no external forces on the molecule. Hence the only forces acting are the internal bonding forces between adjacent atoms. Even simple molecules like these can bend or rotate. To simplify things, we will look only at the stretch or compression of the linear bonds between adjoining atoms. Our goal will be to find what are called the *normal modes* of oscillation, a term that we will define later.

   A diatomic molecule

We will illustrate the method by giving many of the details of the analysis of a diatomic molecule, and then we will leave it to you to analyze more complicated molecules. Consider a molecule such as oxygen (O_2), which has two atoms. We will assume that this diatomic molecule and its individual atoms are constrained to move on a line, as is indicated in Figure 1. Let x_1 and x_2 be the coordinates of the two atoms with respect to a fixed, but otherwise arbitrary origin. We are concerned with oscillations that are much smaller than the usual distance between the atoms, so we may assume that $x_1 < x_2$ at all times.
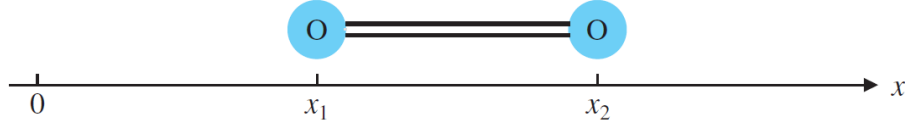

Figure 1: The oxygen molecule, containing two atoms of oxygen.

We will also assume that the atoms in the molecule act like two particles which are connected by a spring. A spring has an equilibrium position, but this is not true for the individual atoms in a molecule. Instead there is an equilibrium distance d between the atoms called the **equilibrium bond length**. When $x_2 - x_1 = d$, the force between them is zero. For small displacements, the force is proportional to the amount that the distance between the atoms differs from the equilibrium distance. Thus, the force on the first atom with displacement x_1 is

$$F_1 = k(x_2 - x_1 - d),$$

where k is the bond constant. If $x_2 - x_1 > d$, the force is positive, which draws the first atom to the right; if $x_2 - x_1 < d$, the force is negative and the first atom is being forced to the left.

Similarly, the force acting on the second atom is

$$F_2 = k(x_1 - x_2 + d).$$

Notice that $F_2 = -F_1$. This means that the two atoms are attracted to each other when the distance between them is greater than d, and they are repelled from each other when their separation is less than d. In addition, the sum of the forces is 0, so the total force on the molecule is 0. The result is that the motion of the molecule as a whole is purely inertial. According to Newton's laws, it moves along the line with constant velocity.

If we assume that the atoms are of equal mass, then according to Newton's second law, the motion of the atoms is governed by the following system of second-order differential equations:

$$mx_1'' = F_1 = k(x_2 - x_1 - d), \tag{1a}$$
$$mx_2'' = F_2 = k(x_1 - x_2 + d). \tag{1b}$$

The differential equations in (1) are linear, second-order equations. The system would be homogeneous except for the presence of d. We can take care of that by making a change of variables. Introduce the modified displacements

$$y_1 = x_1 \quad \text{and} \quad y_2 = x_2 - d \quad \text{or}$$
$$x_1 = y_1 \quad \text{and} \quad x_2 = y_2 + d$$

If we also divide each equation by m, then the system (1) becomes the homogeneous system

$$y_1'' = \frac{k}{m}(y_2 - y_1), \tag{2a}$$
$$y_2'' = \frac{k}{m}(y_1 - y_2). \tag{2b}$$

We can write this in matrix form. If we introduce the matrix

$$K = \begin{pmatrix} -\dfrac{k}{m} & \dfrac{k}{m} \\ \dfrac{k}{m} & -\dfrac{k}{m} \end{pmatrix}$$

and let $\mathbf{y} = (y_1, y_2)^T$ be the vector of displacement, the system becomes

$$\mathbf{y}'' = K\mathbf{y} \tag{3}$$

This is a second-order system. We can write this as a more familiar first-order system if we let $v_1 = x_1' = y_1'$ and $v_2 = x_2' = y_2'$ denote the velocities of the two atoms. Then the second-order system in (2) is equivalent to the first-order system

$$y_1' = v_1, \qquad v_1' = \frac{k}{m}(y_2 - y_1), \tag{4a}$$

$$y_2' = v_2, \qquad v_2' = \frac{k}{m}(y_1 - y_2). \tag{4b}$$

The first-order system can be written in matrix form in the standard way. Let

$$\mathbf{u} = \begin{pmatrix} y_1 \\ y_2 \\ v_1 \\ v_2 \end{pmatrix} \quad \text{and} \quad A = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -\frac{k}{m} & \frac{k}{m} & 0 & 0 \\ \frac{k}{m} & -\frac{k}{m} & 0 & 0 \end{pmatrix}$$

Then the system (4) can be written as

$$\mathbf{u}' = A\mathbf{u}. \tag{5}$$

Of course, the systems in (3) and (5) are equivalent. A solution $\mathbf{y}(t)$ to (3) leads to a solution $\mathbf{u}(t)$ to (5) in the way outlined in the previous paragraph. On the other hand, a solution $\mathbf{u}(t)$ to (5) leads to a solution to (3) by taking $\mathbf{y}(t) = (u_1(t), u_2(t))^T$. We could, therefore, solve the second-order system (3) by solving the more familiar first-order system (5). However, a better way is to use what we know about first-order systems to motivate a solution procedure for the second-order system.

We have learned to solve first-order systems like (5) by looking for exponential solutions. However, if $\mathbf{u}$ is exponential, then the vector, $\mathbf{y}(t) = (u_1(t), u_2(t))^T$, consisting of the first two components of $\mathbf{u}$ is also exponential. So let's look for an exponential solution, $\mathbf{y}(t) = e^{\lambda t}\mathbf{w}$, to (3). Substituting into the left- and right-hand sides of (3), we get

$$\mathbf{y}'' = e^{\lambda t}\lambda^2\mathbf{w} \quad \text{and} \quad K\mathbf{y} = e^{\lambda t}K\mathbf{w}.$$

Thus the exponential function $\mathbf{y}(t) = e^{\lambda t}\mathbf{w}$ will satisfy (3) provided $K\mathbf{w} = \lambda^2\mathbf{w}$. This means that we need λ^2 to be an eigenvalue of K with $\mathbf{w}$ an associated eigenvector.

Let's turn that around. Suppose that σ is an eigenvector of K, and $\mathbf{w}$ is an associated eigenvector. If $\sigma \neq 0$, then σ has two square roots, $\pm\sqrt{\sigma}$. Consequently, the functions

$$\mathbf{y}_1(t) = e^{\sqrt{\sigma}t}\mathbf{w} \quad \text{and} \quad \mathbf{y}_2(t) = e^{-\sqrt{\sigma}t}\mathbf{w}$$

as solutions to (3).

The case when the eigenvalue $\sigma = 0$ is special, since 0 has only one square root. However, we would still expect there to be two corresponding solutions. Notice that the eigenspace of $\sigma = 0$ is just the nullspace of K, so an eigenvector $\mathbf{w}$ satisfies $K\mathbf{w} = 0$. If $f(t)$ is any function of t, and we set $\mathbf{y}(t) = f(t)\mathbf{w}$, then $K\mathbf{y} = 0$. The function $\mathbf{y}(t)$ will be a solution of equation (3) provided that $\mathbf{y}'' = 0$. Notice that $\mathbf{y}'' = f''(t)\mathbf{w}$, so we need the function f to satisfy $f'' = 0$. This is true for any function of the form $f(t) = C_1 + C_2 t$. To sum up, if $\sigma = 0$ is an eigenvalue of K, and $\mathbf{w}$ is in the nullspace of K, then any function of the form $\mathbf{y}(t) = (C_1 + C_2 t)\mathbf{w}$, where C_1 and C_2 are arbitrary constants is a solution to (3).

We are now ready to analyze the oxygen molecule.

(1) Show that the characteristic equation for the matrix K is $p(\sigma) = \sigma(\sigma + 2k/m)$, so the eigenvalues of K are $\sigma_1 = -\omega^2$, where $\omega = \sqrt{2k/m}$, and $\sigma_2 = 0$.

(2) Show that the vector $\mathbf{w}_2 = (1, 1)^T$ is an eigenvector associated with $\sigma_2 = 0$, and that the corresponding motion of the molecule is

$$\mathbf{y}(t) = (y_0 + v_0 t)\begin{pmatrix} 1 \\ 1 \end{pmatrix},$$

where y_0 and v_0 are arbitrary constants. Show that in terms of the original displacements this motion is described by $x_1(t) = y_0 + v_0 t$ and $x_2(t) = (y_0 + d) + v_0 t$. Thus the molecule moves rigidly along the line to which it is constrained with constant velocity v_0. This is the **inertial mode** of the motion.

(3) Show that the vector $\mathbf{w}_1 = (1, -1)^T$ is an eigenvector of K associated with $\sigma_1 = -\omega^2$. Show, using Euler's formula, that the corresponding motion of the molecule can be written as

$$\mathbf{y}(t) = C \cos(\omega t - \phi) \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

The vector

$$C = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

is called the **vector of amplitudes** for the oscillation and ϕ is called the **phase**. Describe this motion. Oscillatory motions such as this are called **normal modes** of oscillation of the molecule.

The displacements x_1 and x_2 are plotted over two periods ($T = 2\pi/\omega$) of oscillation in Figure 2. For convenience we have set the phase $\phi = 0$, and we have chosen the vector of amplitudes small enough to ensure that $x_1(t) < x_2(t)$. This plot displays the essential features of the normal mode.
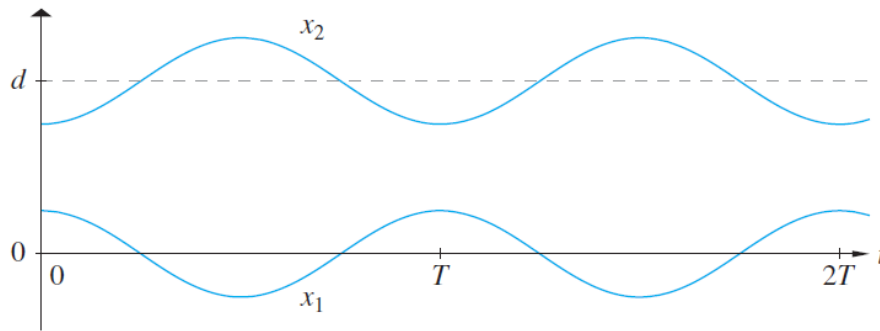

Figure 2: The stretching mode for an oxygen molecule.

A linear triatomic molecule

Admittedly there are easier ways to find the oscillations of a diatomic molecule. However the method we have used pays off when there are three or more atoms in the molecule. We will set up the equations for a linear triatomic molecule (such as CO_2). See Figure 3. Numbering the atoms from one to three, starting from the left, we have three position coordinates x_1, x_2, and x_3. We will assume that the oscillations are very small, so that we always have $x_1 < x_2 < x_3$.
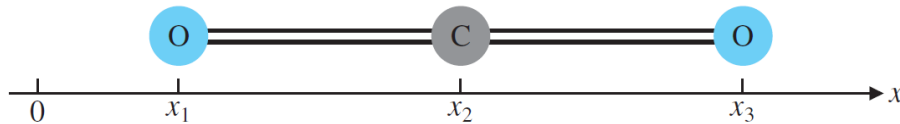

Figure 3: A molecule of carbon dioxide.

The binding forces between the atoms are similar in nature to what we found for the diatomic molecule. Thus, there is an equilibrium bond length d_{12} between atoms 1 and 2, and an equilibrium bond length d_{23} between atoms 2 and 3. We allow for the possibility that each atom is different, and therefore each has a different mass. We also assume that the bond constants for the binding forces are different. Let k_{12} be the bond constant for the force between atoms 1 and 2, and k_{23} that for the force between atoms 2 and 3.

(4) Show that the equations of motion for the three atoms are

$$\begin{aligned}
m_1 x_1'' &= k_{12}(x_2 - x_1 - d_{12}), \\
m_2 x_2'' &= -k_{12}(x_2 - x_1 - d_{12}) + k_{23}(x_3 - x_2 - d_{23}), \\
m_3 x_3'' &= -k_{23}(x_3 - x_2 - d_{23}).
\end{aligned}$$

Show that we can reduce this system to a homogeneous system by choosing the modified dis-

placements $y_1 = x_1$, $y_2 = x_2 - d_{12}$, and $y_3 = x_3 - d_{12} - d_{23}$, and that the resulting equations are

$$y_1'' = \frac{k_{12}}{m_1}(y_2 - y_1),$$

$$y_2'' = -\frac{k_{12}}{m_2}(y_2 - y_1) + \frac{k_{23}}{m_2}(y_3 - y_2),$$

$$y_3'' = -\frac{k_{23}}{m_3}(y_3 - y_2).$$

Find the matrix K for which the above system can be written as $\mathbf{y}'' = K\mathbf{y}$.

From this point on the analysis of the modes of motion of a carbon dioxide molecule can be done either analytically or numerically. For either approach you should notice that the two oxygen atoms have the same mass, so $m_3 = m_1$, and the two bond constants are the same so $k_{12} = k_{23} = k$. With these simplifications the modes can be found algebraically, but the computation cannot be called trivial.

To facilitate the numerical approach we need to give you the data on the masses and bonding constants. First, however, we need to worry about units. Any consistent set of units could be used, but for problems involving atoms it is not usually convenient to use the International System. The set of "atomic units" is most appropriate. The atomic unit of mass is the mass of the electron. It is denoted by m_e, and 1 $m_e = 9.1091 \times 10^{-31}$ kg. The unit of length is the radius of the orbit of the lowest energy electron in the Bohr model of the hydrogen atom. It is called the **bohr** or the **bohr radius**, it is denoted by a_o, and 1 $a_o = 5.29167 \times 10^{-11}$ m. Finally, the atomic unit of time is the period of the the lowest energy electron in the Bohr model of the hydrogen atom. It is denoted by a_u, and 1 $a_u = 2.41888 \times 10^{-17}$ s.

In these units, the mass of a carbon atom is $m_2 = 21,876$ m_e and the mass of an oxygen atom is $m_1 = m_3 = 29,168$ m_e. The carbon-oxygen binding force constant in CO_2 is $k_{12} = k_{23} = k = 0.4758$ in atomic units.

(5) Calculate the eigenvalues and eigenvectors of K.

(6) Describe the inertial mode for a CO_2 molecule.

(7) There are two normal modes of oscillation for the CO_2 molecule. Describe the motion of each in terms of its frequency and vector of amplitudes. One mode might be called the symmetric stretch, and the other the antisymmetric stretch. Figure out which is which.

(8) For each normal mode plot the displacements x_1, x_2, and x_3 on a single graph versus time. You need to know that the equilibrium bond length of each CO in CO_2 is 2.2 a_o. Choose the multiplicative factor in the vector of amplitudes small enough to ensure that $x_1(t) < x_2(t) < x_3(t)$, and large enough to be easily visible, and set the phase equal to 0. Use the same time interval for both modes. Choose it to span two periods for the slowest oscillation. These graphs display the nature of the modes quite nicely.

Optional Problem: *A more complicated example*

Larger molecules have more oscillatory normal modes. For example, cyanoacetylene, HCCCN, is a linear molecule with five atoms (see Figure 4). The normal modes can be found using the method used for O_2 and CO_2. Since HCCCN has five molecules, we expect that there will be four normal modes of oscillation in addition to the inertial mode. Reasonable choices of the force constants in atomic units are: $k_{HC_1} = 0.378$, $k_{C_1 C_2} = 1.087$, $k_{C_2 C_3} = 0.441$, and $k_{C_3 N} = 1.031$. The mass of a hydrogen atom is 1,823 m_e and the mass of a nitrogen atom is 25,522 m_e. For HCCCN, the bond lengths are from left to right: HC_1 2.0281 a_o, $C_1 C_2$ 2.2716 a_o, $C_2 C_3$ 2.6664 a_o, and $C_3 N$ 2.1776 a_o. Notice that the two CC lengths and the two CC force constants are not close to being equal. This reflects the fact that the $C_1 C_2$ bond is a triple bond, while the $C_2 C_3$ bond is a single bond, as indicated in Figure 4.
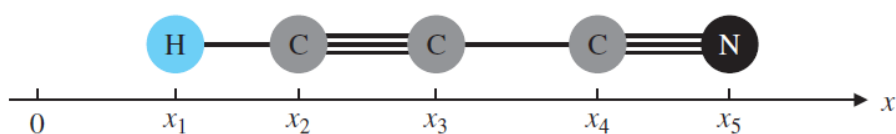

Figure 4: A molecule of cyanoacetylene, HCCCN.

(9) Use a computer to calculate the inertial mode and the normal modes for the stretching motions in cyanoacetylene. Plot the motions of the atoms in each normal mode.