THE VIBRATIONS OF MOLECULES II
THE CARBON DIOXIDE MOLECULE©

Student Instructions

by

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This document contains the instructions for the Mathcad file entitled co2run.mcd. The equations in this document are bitmap images and not Mathcad active. The Mathcad active equations are found in co2run.mcd. Students should first complete the exercises for the simple harmonic oscillator that are found in horun.mcd and its accompanying instructional file hoins.mcd.

In this lesson we will examine the mathematical basis for representing the vibrations of CO_2. We will assume that the force constant for each C-O bond is k. The molecule is arranged along the x axis with coordinates of the three atoms being x_1, x_2, and x_3, the left oxygen, the carbon, and the right oxygen respectively. Note that $m_1 = m_3$. Sketch the molecule.

Goal: To explore classical harmonic oscillator motion in a linear triatomic molecule.

Objectives:
1. To use matrix algebra to transform between coordinate systems used to represent a molecule
2. To write the Laplacian and equations of motion for a linear triatomic molecule.
3. To explain the motion of triatomic molecules in terms of the potential and kinetic energy contributions from each atom.

Prerequisites:
1. Successful completion of hoins.mcd and horun.mcd exercises;
2. Mathcad 6.0+ is required to to solve the differential equations;
3. Differential calculus is needed in order to take the required derivatives. Students should understand what "to solve a differential equation" means.
4. Only elementary level skill with Mathcad is required to use the co2run.mcd document. More advanced skill would be required to author documents of this type.

The kinetic energy is the sum of the kinetic energy contributed by each atom:

$$T = \frac{1}{2}\left(m_1\dot{x}_1^2 + m_2\dot{x}_2^2 + m_1\dot{x}_3^2\right) \qquad (1)$$

The extent Q_1 that the left bond is stretched or compressed compared to its equilibrium bond length of r_e is

$$Q_1 = x_2 - x_1 - r_e \qquad (2)$$

Similarly for Q_2

$$Q_2 = x_3 - x_2 - r_e \qquad (3)$$

Where at equilibrium $x_2 - x_1 = r_e$ and $x_3 - x_2 = r_e$

Taking the time derivatives we get

$$\dot{Q}_1 = \dot{x}_2 - \dot{x}_1 \quad \text{and} \quad \dot{Q}_2 = \dot{x}_3 - \dot{x}_2 \qquad (4)$$

The center of mass of the molecule is given by $C = \frac{\sum_i m_i x_i}{\sum_i m_i}$

The time derivative of the center of mass yields equation 5.

$$\frac{m_1\dot{x}_1 + m_2\dot{x}_2 + m_3\dot{x}_3}{M} = \dot{C} \qquad (5)$$

Next we write the potential energy in terms of the stretching of each bond. Notice how Hooke's law is used here.

$$V = \frac{1}{2}\left(k\, Q_1^2 + k\, Q_2^2\right) \qquad (6)$$

Above we described the kinetic energy T in terms of x coordinates, and the potential energy V in terms of Q coordinates. In order to obtain the equations of motion we must describe T and V in the same coordinates. Since we will use the Q coordinates below, we must obtain both T and V in terms of the Q's. This can be done by using a matrix transformation. The matrix equation to accomplish this is

$$\begin{pmatrix} \dot{Q}_1 \\ \dot{Q}_2 \\ \dot{C} \end{pmatrix} = \begin{pmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ \frac{m_1}{M} & \frac{m_2}{M} & \frac{m_3}{M} \end{pmatrix} \begin{pmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \end{pmatrix} \qquad (7)$$

To obtain the x coordinates in terms of the Qs we invert the 3x3 matrix and multiply each side of equation 7 on the left by this inverse to get:

$$\begin{pmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \end{pmatrix} = \frac{1}{M} \begin{pmatrix} -m_1 - m_2 & -m_1 & M \\ m_1 & -m_1 & M \\ m_1 & m_1 + m_2 & M \end{pmatrix} \begin{pmatrix} \dot{Q}_1 \\ \dot{Q}_2 \\ \dot{C} \end{pmatrix} \qquad (8)$$

Where $M = 2m_1 + m_2$. Recall that $m_1 = m_3$.

Question 1. Write the expression for the $\dot{x}$'s as a function of $\dot{Q}$'s and $\dot{C}$.

The kinetic energy as a function of the $\dot{Q}$'s can be obtained by substituting the $\dot{x}$'s from the above matrix equation into equation 1.

After considerable algebra we get equation 9.

$$T = \frac{1}{2}\frac{m_1(m_1+m_2)}{M}\left(\dot{Q}_1^2+\dot{Q}_2^2\right)+\frac{m_1^2}{M}\dot{Q}_1\dot{Q}_2+\frac{1}{2}m\dot{C}^2 \qquad (9)$$

Question 2. Does the kinetic energy depend on the center of mass? What coordinates are essential for describing this system of three atoms? Complete the algebraic step leading from equation 1 to equation 9. This is not a trivial algebraic process. Be careful.

Collecting the constants into B_{11} and B_{12} we can rewrite the kinetic energy as

$$T = B_{11}(\dot{Q}_1^2+\dot{Q}_2^2) + B_{12}\dot{Q}_1\dot{Q}_2 \qquad (10)$$

which with the potential energy in terms of the Q's

$$V = \frac{1}{2}k(Q_1^2+Q_2^2) \qquad (11)$$

can be substituted into Lagrange's differential equation (12), first for Q_1 then for Q_2 and then for Cdot.

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{Q}_i}-\frac{\partial L}{\partial Q_i}=0 \qquad (12)$$

to give the following equations of motion

$$2B_{11}\ddot{Q}_1 + B_{12}\ddot{Q}_2 + kQ_1 = 0 \qquad (13)$$

$$B_{12}\ddot{Q}_1 + 2B_{11}\ddot{Q}_2 + kQ_2 = 0 \qquad (14)$$

$$m\dot{C}^2 = 0 \qquad (15)$$

Equation 15 does not contribute to the equations of motion describing the position of the oxygens. We will thus solve equations 13 and 14 as a coupled pair of differential equations

Question 3. Write the Lagrangian for the CO_2 molecule.

Question 4. Complete the details of obtaining equations 13 and 14.

Equations 13 and 14 cannot be solved by MATHCAD in this form shown above. We must first solve them for each of the second derivatives in order to use the rkfixed Mathcad function. The rkfixed function gives us a numerical solution to the set of differential equations.

$$\ddot{Q}_1 = \frac{\frac{2 B_{11} k}{B_{12}} Q_1 - k Q_2}{\left[B_{12} - \frac{4 B_{11}^2}{B_{12}} \right]} \qquad (16)$$

$$\ddot{Q}_2 = \frac{\frac{k B_{12}}{2 B_{11}} Q_1 - k Q_2}{\left[2 B_{11} - \frac{B_{12}^2}{2 B_{11}} \right]} \qquad (17)$$

The values of k and the masses of the atoms are used with these equations in the computational document where the differential equations are solved.

Question 5: Complete the details of obtaining equations 16 and 17 from equations 13 and 14.

EXERCISE 1

The input to the differential equations routine has some adjustable constants. We must set values of the masses of the atoms m_1 and m_2 which can be taken as 16 and 12 for O (m_1 and m_3) and C (m_2) respectively. The value of the force constant should be set to 200. The column matrix **Q** in co2run.mcd gives the initial values of the Q's and their initial velocities:

$$\mathbf{Q} = \begin{pmatrix} Q_1 \\ \dot{Q}_1 \\ Q_2 \\ \dot{Q}_2 \end{pmatrix}$$

Set each initial velocity equal to 3 and each initial position equal to zero. Calculate all four pages of the document. Which vibrational mode does the chosen initial conditions simulate? For the animation part place the cursor (red cross) just to the right of the top of the animation plot and click on Graphics and Animation and create. Then with the mouse block out the portion of the picture you wish to animate. If necessary press the lightbulb button to activate the automatic mode. The animation will now be recorded and when it is complete a window will appear at the left for the playback feature. Clicking on the lower left button in this window will activate the playback.

Note the Fourier transform of the motion of Q_1 on the last page. This is a plot in frequency space of the vibrational frequencies contained in this motion.

EXERCISE 2

Go to the Q matrix and change one of the derivatives from 3 to -3. Repeat the calculations. Has the frequency become larger or smaller?
Which vibrational mode does this represent?

EXERCISE 3

Go again to the Q matrix and change the initial POSITION Q_1 to 2 and change the initial VELOCITY for Q_2 to 3. Repeat the calculation. Note that the motion becomes a mixture of the two modes and appears to be haphazard. But the Fourier transform can display two frequencies (even though the phasing of the maxima is not great).

Question 6: What is the physical meaning of having initial value of Q for particle 1 equal to 3 and the initial velocity of particle 1 equal to zero and at the same time have the initial position value of Q for particle 2 equal to zero and the corresponding velocity for this coordinate equal to 3?