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Computers in Chemistry

A Computational Exercise Illustrating Molecular Vibrations and Normal Modes

SUSAN B. REMPE* AND HANNES JÓNSSON
Department of Chemistry
University of Washington
Seattle, WA 98195
rempe@euclid.chem.washington.edu, hannes@u.washington.edu

At the end of the exercise, the students should be better prepared for encounters with molecular vibration in their future work.

Molecular vibration plays an important role in chemistry, both in chemical reactions and in the characterization and measurement of molecular structure and bonding. Normal modes provide the conceptual framework for understanding molecular vibrations. For example, the analysis of infrared spectra, an important tool for chemists, relies heavily on the concept of normal modes; yet, undergraduate students, even chemistry majors, seldom gain a thorough understanding of normal modes through the traditional chemistry curriculum. In fact, the most commonly used physical chemistry textbooks give only a cursory introduction to this concept, leaving out the substantive development. This occurs presumably because normal modes emerge from a multistepped mathematical analysis of the molecular dynamics. While the mathematical

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skill needed for each step typically has been covered in an introductory calculus course, the full development is a lengthy process and skipped in the texts. Thus, students have little opportunity to develop a sound conceptual understanding of “vibrational modes” and “fundamental vibrational frequencies,” even though they inevitably encounter these terms in their future work.

Introduction

In a chemistry computer laboratory course at the University of Washington, briefly described elsewhere [1], one of the exercises features a study of molecular vibrations by various computer calculations and simulations. In this exercise, the students first perform simulations motivating the introduction of normal modes, then complete analyses defining and calculating the modes, and finally explore, again by simulation, the strengths and limitations of the normal-mode description of molecular vibrations. This is accomplished during a four-hour laboratory period utilizing computer software with high-level mathematical and graphics capabilities. We present here our approach to using the computer as a tool for teaching this concept and discuss the calculations carried out by the students during the exercise. We note that a great deal of effort has been devoted to the use of computers in the undergraduate chemistry curriculum with most of that effort focused on electronic structure calculations and molecular modeling [2]. Computer software designed for a special topics graduate course on molecular vibrations has been described [3], as well as software for animating molecular vibrations on a Macintosh computer [4].

In the calculations described here, the students independently program the relevant equations using a high-level programming environment. This reduces the mathematical tedium, yet retains the essential hands-on experience. To maximize the conceptual development and minimize the complexity of the calculations and graphics, most of the exercise deals with a simple triatomic molecule confined to move in one dimension. We choose to model the potential energy interaction between each bonded pair of atoms by a Morse function. A schematic overview of the calculation and analysis follows:

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A. Visualization of the atomic interactions by drawing a contour plot and a three-dimensional image of the potential energy surface.

B. Calculation of the classical-mechanical time evolution of the molecular coordinates and velocities starting with arbitrary displacements of the atoms from their optimal positions. The molecular vibration is visualized by superimposing the classical trajectory on the contour plot of the potential energy surface and by animating the atomic motion.

C. Extraction of frequency components by Fourier expanding the atomic velocities and thereby identification of certain distinct and prominent frequencies in the atomic motion.

D. Development of a harmonic approximation to the interaction potential by Taylor expansion and calculation of the normal modes by solving the eigenvalue problem. The eigenvalues are then compared with the peaks in the Fourier expansion of the classical trajectory.

E. Calculations of classical trajectories starting with initial atomic displacements of varying magnitude but in the direction of each normal-mode eigenvector. Again the molecular vibration is visualized both by drawing the trajectory over the potential energy contour plot and by animating the atomic motion.

Finally, if time permits, the students can easily extend the calculation to larger molecules in one dimension or use Mathematica modules, written by us, to calculate and animate normal modes of triatomic molecules in three dimensions: CO_2, a linear molecule, and H_2O, a bent molecule.

All these calculations are done with the program Mathematica [5] running on a color graphics workstation. The students generate the classical trajectories using code partially developed by them and used in a previous exercise involving reaction dynamics [1]. After producing the classical trajectories, the analysis requires only five input commands to the program! Each graphics display requires one command except for the animation, which is more tedious. Code prewritten by us to animate the molecular vibrations is included as part of the program that creates the classical trajectories. With these tools, the students can then explore variants of the calculations detailed in the handout. For example, the students can change the masses, the potential

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parameters, and the initial atomic displacements and study the effects, watching for such things as intramolecular vibrational energy transfer [6], transitions from normal to local mode behavior [7], and the onset of chaotic trajectories [8]. Furthermore, the students can extend the calculation to study vibrations of more complex molecules. We point out that other high-level mathematical analysis and graphics programs such as Maple or Matlab [9, 10] can be used to carry out the calculations described here instead of Mathematica, and powerful personal computers can be used instead of computer workstations.

Calculation and Analysis

The Atomic Interaction

The calculations are performed on a simple model of a triatomic molecule confined for simplicity to one dimension along the molecular axis. Potential parameters and atomic masses are chosen to mimic a CO_2 molecule. In atomic mass units, the oxygen atoms take mass $m_A = m_C = 16$ and the carbon atom $m_B = 12$. The Cartesian coordinates x_A, x_B and x_C identify the instantaneous position of each atom in space. Because the potential energy of an isolated molecule depends only on the relative positions of the atoms, the most convenient set of coordinates for describing the potential are internal coordinates, that is, coordinates unaffected by translation and rotation of the molecule as a whole. Detailed discussions of internal coordinates for more complex molecules can be found in the literature [11, 12]. The two internal coordinates describe the instantaneous separation between atoms A and B, $r_{AB} = x_B - x_A$, and between atoms B and C, $r_{BC} = x_C - x_B$ (see Figure 1a). The interaction between each chemically bonded pair of atoms is described by a Morse potential function,

$$V_{AB}(r) = d_{AB}\left(e^{-2a_{AB}(r-b_{AB})} - 2e^{-a_{AB}(r-b_{AB})}\right)$$

and

$$V_{BC}(r) = d_{BC}\left(e^{-2a_{BC}(r-b_{BC})} - 2e^{-a_{BC}(r-b_{BC})}\right) \tag{1}$$

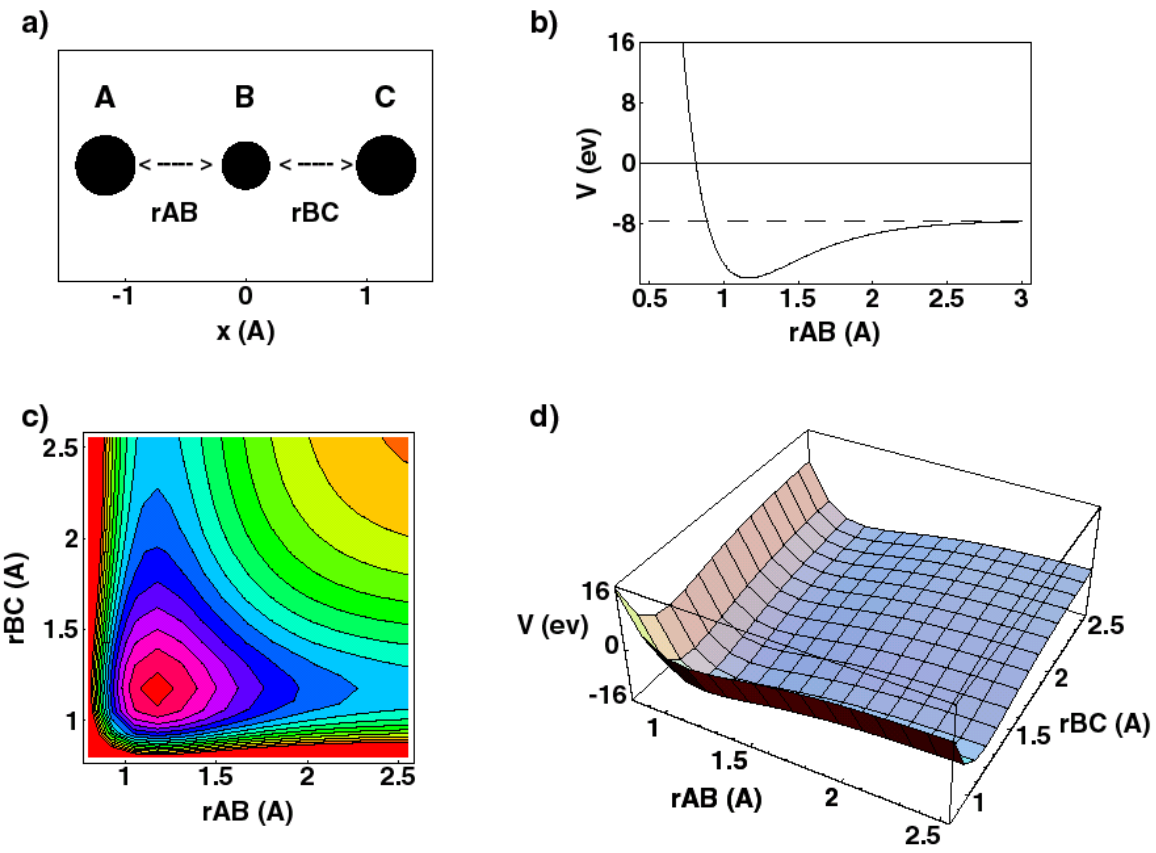

FIGURE 1. VISUALIZING THE MODEL POTENTIAL FOR THE MOLECULE IN VARIOUS WAYS: (a) DEFINITION OF THE CARTESIAN COORDINATES x_i AND INTERNAL COORDINATES r_{AB} AND r_{BC}, (b) TOTAL POTENTIAL ENERGY PLOTTED AS A FUNCTION OF BOND LENGTHS r_{AB} WITH r_{BC} HELD CONSTANT, (c) A CONTOUR PLOT OF THE POTENTIAL ENERGY SURFACE, (d) A THREE-DIMENSIONAL ROTATABLE PLOT OF THE POTENTIAL ENERGY SURFACE.

The total potential energy is the sum of the two Morse potentials

$$V\left(r_{AB}, r_{BC}\right) = V_{AB}\left(r_{AB}\right) + V_{BC}\left(r_{BC}\right) \tag{2}$$

In the Morse potential energy functions, the parameters d_{AB} and d_{BC} give the well depth, b_{AB} and b_{BC} the positions of minimum energy for each bonded atomic pair (the equilibrium bond lengths), and a_{AB} and a_{BC} the exponential decay length (see Figure 1b). The values of the parameters in the potential functions are chosen to be $d_{AB} = d_{BC} = 7.65$ eV, $b_{AB} = b_{BC} = 1.162$ Å, and $a_{AB} = a_{BC} = 2.5$ Å^{-1}.

To visualize the atomic interaction potentials, the students generate a colored contour plot (Figure 1c) and three-dimensional plot (Figure 1d) of the potential energy surface.

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The main utility of the three-dimensional surface plot, with its free viewing angle and revolvable image, lies in its ability to clarify the meaning of the contour plot. Chemists routinely use contour plots to visualize the energetics of molecular systems, even complex ones, in which case the two 'most important' degrees of freedom become the parameters in the contour plot. An important aspect of this exercise is to make the chemistry student familiar with and able to interpret such contour plots.

Molecular Dynamics Simulation

The vibrational motion of the CO_2 atoms interacting via Morse functions is simulated using classical-mechanical equations of motion. Whereas classical and quantum mechanics lead to the same result for the normal-mode vibrational frequencies, the classical treatment is more intuitive. Furthermore, when the system of interest is composed of heavy atoms at high enough energies or temperatures, then it is sufficiently accurate to neglect quantum effects [13] and calculate the time evolution of a molecule using the classical equation of motion obtained from Newton's second law

$$F_i = m_i \frac{dv_i(t)}{dt} \text{ where } v_i = \frac{dx_i(t)}{dt} \qquad (3)$$

Here i denotes any one of the atoms, A, B or C. F_i is the force acting on atom I, m_i the atomic mass, and v_i the velocity. The force is obtained from the potential energy function by taking the partial derivative with respect to the atomic coordinate.

$$F_i = -\frac{\partial V}{\partial x_i} \qquad (4)$$

To simulate the molecular vibration, equation 3 must be solved for the trajectory $x_i(t)$ of each atom. This is accomplished using a simple finite-difference scheme called the velocity Verlet algorithm [14]. In a previous exercise, the students develop a program in Mathematica for carrying out simulations of chemical reaction dynamics using the algorithm [1]. In this exercise, they apply the same code to calculate the trajectory of molecular vibrations.

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Time is discretized in the finite-difference algorithm so that it evolves in discrete but small steps. In the velocity Verlet algorithm, the coordinates and velocities of the atoms at each time step are generated by iteratively applying the equations

$$x_i(t+h) = x_i(t) + hv_i(t) + \frac{h^2 F_i(x_i(t))}{2m_i} \tag{5}$$

$$v_i(t+h) = v_i(t) + \frac{h(F_i(x_i(t+h)) + F_i(x_i(t)))}{2m_i} \tag{6}$$

Here h is the size of the time step. These equations are approximate. A Taylor series analysis shows that terms of third order and higher in h have been neglected.

Denoting the atomic coordinate at time $t = (n - 1) \times h$ (the time elapsed after n time steps) as $x_i[n]$ and the velocity as v_i[n], the velocity Verlet algorithm can be written schematically as follows:

Given $x_i[n]$ and $v_i[n]$ and an expression for $F_i(x_i)$:
Step 1. Calculate $x_i[n + 1]$ for each atom using equation 4.
Step 2. Evaluate the force on each atom $F_i(x_i[n + 1])$.
Step 3. Calculate $v_i[n + 1]$ for each atom using equation 5.
Return to Step 1 and repeat.

It is convenient to evaluate the forces by first differentiating the Morse potential expression, equation 1, with respect to each of the two internal coordinates and then applying the chain rule to calculate the derivative of the potential function with respect to the atomic coordinates. The derivatives are evaluated at the new position, $x_i[n + 1]$, of each atom. For example, the expression for the force on atom B, which involves both internal coordinates, becomes

$$F_B = -\frac{\partial V}{\partial x_B} = -\frac{\partial V}{\partial r_{AB}}\frac{\partial r_{AB}}{\partial x_B} - \frac{\partial V}{\partial r_{BC}}\frac{\partial r_{BC}}{\partial x_B} = -\frac{\partial V}{\partial r_{AB}} + \frac{\partial V}{\partial r_{BC}}$$

This classical simulation scheme can be coded in Mathematica almost directly as written. The functions **dVdrAB** and **dVdrBC** give the derivatives of the potential with

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respect to the internal coordinates. Arbitrary initial values are assigned to coordinates $x_i[0]$ and velocities $v_i[0]$. The main loop advances time by a step *h* in each iteration:

```
Do [{
xA[n+1] = xA[n] + h*vA[n] + h^2*fA[n]/(2*mA),
xB[n+1] = xB[n] + h*vB[n] + h^2*fB[n]/(2*mB),
xC[n+1] = xC[n] + h*vC[n] + h^2*fC[n]/(2*mC),

rAB[n+1] = xB[n+1] - xA[n+1],
rBC[n+1] = xC[n+1] - xB[n+1],

fA[n+1] = dVdrAB[rAB[n+1], rBC[n+1]],
fB[n+1] = -dVdrAB[rAB[n+1], rBC[n+1]] + dVdrBC[rAB[n+1], rBC[n+1]],
fC[n+1] = -dVdrBC[rAB[n+1], rBC[n+1]],
vA[n+1] = vA[n] + h*(fA[n+1] + fA[n])/(2*mA),
vB[n+1] = vB[n] + h*(fB[n+1] + fB[n])/(2*mB),
vC[n+1] = vC[n] + h*(fC[n+1] + fC[n])/(2*mC),
                        },{n,1,nsteps-1,1}] / /N;
```

Here *nsteps* determines the total number of times steps that are generated while the *//N* at the end makes the calculation numerical. This iterative procedure produces a collection of positions and velocities for each atom at each time step, giving a discrete representation of the classical trajectory of the molecule.

The students visualize the simulated molecular motion in various ways. First, using initial conditions of their choice, they generate a graph of the trajectory in the two-dimensional plane of internal coordinates, as shown in Figures 2a and 2b. The graph showing the trajectory $(r_{AB}(t), r_{BC}(t))$ on top of the contour plot relates the dynamics to the energetics. Secondly, they animate the dynamics of the atoms. The initial frame in the animation series is shown in Figure 2a. Finally, a graph of the velocity of an atom as a function of time is created. The velocity of atom A is shown in Figure 2c. By displaying these different images of the molecular motion simultaneously on the screen, the students develop a better understanding of how each one represents the dynamics. The images describe the same dynamical evolution of the molecule, but in different and complementary ways.

The Dominant Frequencies

The molecular motion in Figures 2a–c appears complex and irregular. To gain insight into the complex motion, temporal information from an atomic trajectory is resolved into frequency information. A Fourier expansion of one atomic velocity, $v_i(t)$, yields

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the frequency components of the atomic motion and their relative prominence. A full calculation of the power spectrum would require the sum over the Fourier expansion of all the atomic velocities [15], but is not necessary when the goal is simply to identify the dominant frequency components of the motion.

The Fourier expansion is straightforward within Mathematica. First, a list is created containing the atomic velocity at each time step. For example, the collection of velocities from atom A can be put into list “vAlist”,

```
vAlist = Table[vA[n],{n,1,nsteps}]
```

After Fourier expanding the elements of the list, the coefficients for the frequencies are stored in a new list,

```
freqdata = Abs[Fourier[vAlist]]
```

which can easily be graphed. The results of Fourier expanding the trajectory shown in Figures 2a–c is plotted in Figure 2d.

The graph in Figure 2d reveals that the atomic motion contains two dominant components, one at about twice the frequency of the other. Less prominent peaks appear at positions corresponding to sums of the dominant frequencies. Here the initial displacement of the atoms is large, changing the bond lengths up to 0.28 Å. The absolute angular frequencies are obtained from the index n of the frequency component by $\omega_n = (n - 1)2\pi/T$, where T is the total time of the trajectory. For example, frequencies $\omega_{15} = 1840\ \mathrm{cm}^{-1}$ and $\omega_8 = 920\ \mathrm{cm}^{-1}$ dominate the molecular motion illustrated in Figure 2.

Solving for the vibrational motion of the linear triatomic molecule by classical mechanics produces atomic trajectories such as the ones plotted in Figures 2a–c. A Fourier analysis resolves the complex irregular motion into a set of frequency components. The next logical step is to identify the particular vibrational motions, or modes, that correspond to each of the dominant frequencies of the simulated motion. This leads the students to a normal-mode analysis.

Normal-mode Analysis

The equations of motion for the atoms simplify when the potential energy of interaction is harmonic. In such harmonic systems, a linear combination of the atomic

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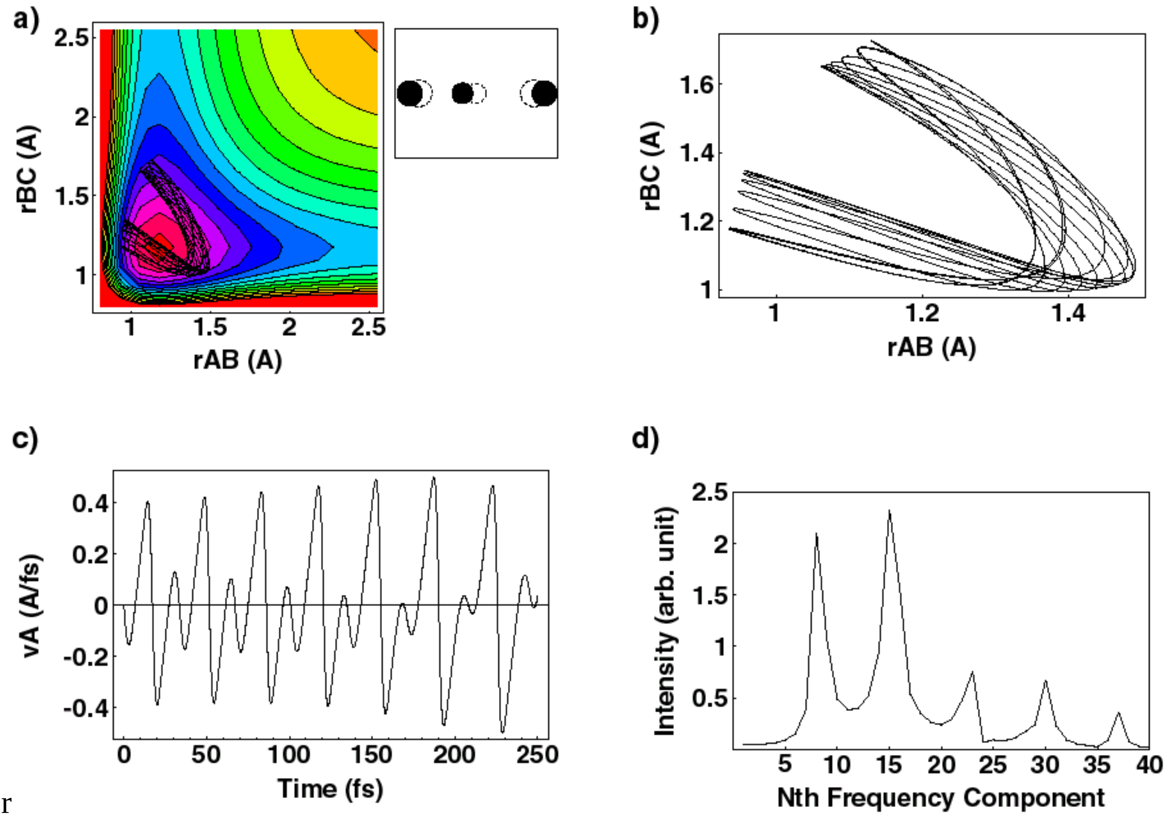

or

FIGURE 2. ILLUSTRATION AND ANALYSIS OF THE TIME EVOLUTION OF THE MOLECULE OVER A 250-fs TIME INTERVAL SIMULATED BY THE VELOCITY VERLET ALGORITHM FOR INITIAL ATOMIC DISPLACEMENTS IN ÅNGSTROMS: $x_A = -0.18$, $x_B = -0.28$, $x_C = 0.21$. (a) THE TRAJECTORY SPECIFIED BY THE INTERNAL COORDINATE PAIRS ($r_{AB}(t)$, $r_{BC}(t)$) PLOTTED OVER THE CONTOUR PLOT OF THE POTENTIAL ENERGY SURFACE. INITIAL ATOMIC POSITIONS APPEAR TO THE RIGHT OF THE CONTOUR PLOT. (b) THE SAME TRAJECTORY AS IN (a) ON A LARGER SCALE. (c) THE VELOCITY OF ATOM A PLOTTED AS A FUNCTION OF SIMULATION TIME. (d) THE FOURIER EXPANSION OF THE VELOCITY OF ATOM A OVER THE SIMULATED TIME INTERVAL. THE TWO LARGE PEAKS INDICATE THE DOMINANT FREQUENCIES OF THE MOLECULAR DYNAMICS, WHICH CORRESPOND APPROXIMATELY TO THE NORMAL MODES OF VIBRATIONAL MOTION SHIFTED DOWN IN FREQUENCY. THE SMALLER PEAKS APPEAR AT SUMS OF THE DOMINANT PEAK FREQUENCIES, CORRESPONDING TO COMBINATIONS OF NORMAL MODE MOTIONS.

coordinates can be defined so that the set of coupled equations (one for each atom) separates into three independent equations, each with an analytical solution corresponding to simple harmonic motion. These linear combinations of atomic coordinates are called normal coordinates. Each normal coordinate describes a collective motion or mode of the molecule during which all atoms vibrate in phase at one frequency. The goal of the normal-mode analysis is to identify the normal coordinates and frequencies of vibrational motion.

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While the interaction between atoms is more realistically described by Morse potentials or functions of similar form, in the immediate vicinity of the equilibrium position, the atomic interactions can be represented by a harmonic approximation to the potential function. To obtain this approximate harmonic potential, the model potential function is expanded in a Taylor series about the equilibrium configuration up to second order in the internal coordinates, r_{AB} and r_{BC}.

A Taylor series expansion is done easily within Mathematica. Let the function **V[rAB,rBC]** be defined as the sum of the two Morse potentials as in equation 2. The Taylor expansion of the potential energy function about the equilibrium geometry in terms of internal coordinates, truncated at the second order term, is obtained by

```
Series [V[rAB, rBC],{rAB,bAB,2},{rBC,bBC,2}]
```

Replacing the bond lengths r_{AB} and r_{BC} with Cartesian coordinates $x_B - x_A$ and $x_C - x_B$, the expression for the harmonic approximation to the real potential becomes a function of the three atomic Cartesian coordinates,

$$V_{harm}\left(x_A, x_B, x_C\right) = V_0 + \tfrac{1}{2}k_{AB}\left(x_B - x_A - b_{AB}\right)^2 + \tfrac{1}{2}k_{BC}\left(x_C - x_B - b_{BC}\right)^2 \qquad (7)$$

where V_0 is the energy of the equilibrium configuration and k_{ij} is the second partial derivative of the full potential with respect to the Cartesian x_i and x_j coordinates evaluated at the equilibrium geometry. These constants, called force constants, can be done by hand or Mathematica can be used to calculate them, provided the potential function V has been defined in terms of Cartesian coordinates. For example, k_{AB} can be found with the Mathematica command

```
D[V[xA,xB,xC],xA,xB]/.{xA → -bAB, xB → 0, xC → bBC}
```

When the potential is harmonic, the equations of motion become linear and the set of coupled equations can be arranged as a matrix equation corresponding to a matrix-eigenvalue problem. For example, Newton's second law in equations 3 and 4 yields this set of coupled linear equations for the motion of three atoms in displacement coordinates, $\Delta x_i = x_i - x_i^0$:

$$\Delta\ddot{x}_A(t) = -\frac{k_{AB}}{m_A}\left(\Delta x_A - \Delta x_B\right)$$

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$$\Delta \ddot{x}_B(t) = -\frac{k_{AB}}{m_B}(\Delta x_B - \Delta x_A) - \frac{k_{BC}}{m_B}(\Delta x_B - \Delta x_C)$$

$$\Delta \ddot{x}_C(t) = -\frac{k_{BC}}{m_C}(\Delta x_C - \Delta x_B) \tag{8}$$

Possible solutions to these equations correspond to motions at a single vibrational frequency ω such that all the atoms vibrate in phase with the same frequency but in different directions and with different amplitudes.

$$\Delta \ddot{x}_A(t) = -\omega^2 \Delta x_A(t)$$

$$\Delta \ddot{x}_B(t) = -\omega^2 \Delta x_B(t)$$

$$\Delta \ddot{x}_C(t) = -\omega^2 \Delta x_C(t) \tag{9}$$

When these solutions are substituted into the equations of motion above (equation 8), the set of coupled equations becomes a matrix-eigenvalue equation.

$$\begin{pmatrix} k_{AB}/m_A & -k_{AB}/m_A & 0 \\ -k_{AB}/m_B & (k_{AB}+k_{BC})/m_B & -k_{BC}/m_B \\ 0 & -k_{BC}/m_C & k_{BC}/m_C \end{pmatrix} \begin{pmatrix} \Delta x_A \\ \Delta x_B \\ \Delta x_C \end{pmatrix} = \omega^2 \begin{pmatrix} \Delta x_A \\ \Delta x_B \\ \Delta x_C \end{pmatrix} \tag{10}$$

The first line comes from the equation of motion of atom A, the second from B, and the third line from the equation of motion for atom C. In Mathematica, the force-constant matrix evaluated at the equilibrium geometry can be generated in this way.

```
matrix =        {{kAB/mA, -kAB/mA, 0},
                {-kAB/mB, (kAB+kBC)/mB, -kBC/mB},
                {0, -kBC/mC, +kBC/mC}}
```

Once the force-constant matrix is defined, the eigenvalue problem can be solved and the normal coordinates and frequencies identified. The solution to the eigenvalue problem is found using one command in Mathematica,

```
Eigensystem[matrix]
```

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The output in this case consists of a set of three eigenvalues, $\{\omega_i^2\}$, and the corresponding eigenvectors. The square root of each eigenvalue gives the angular frequency of classical vibration while the corresponding eigenvector describes the motion in terms of the relative atomic displacements. One eigenvalue is zero (within the accuracy of the numerical calculation) and represents uniform translation of the molecule. The two nonzero frequencies correspond to a lower frequency (1278 cm^{-1}) symmetric motion in which the outer atoms move in the opposite direction and a higher frequency (2448 cm^{-1}) antisymmetric motion in which the two outer atoms move together while the center moves opposite. These two collective oscillatory motions of the molecule, during which the atoms move at one frequency according to relative displacements given by the eigenvector, are the normal modes of vibration. If the molecule were not confined to motion along the molecular axis, then the additional six degrees of freedom available would result in a total of five zero frequencies representing uniform translation of the molecule along each of the coordinate axes, and a total of four nonzero frequencies corresponding to two stretching and two degenerate bending normal modes of vibration.

By making a harmonic approximation to the model potential function, the equations of motion describing the vibrational dynamics simplify into a set of coupled linear equations. Solving the resulting eigenvalue problem defines the normal coordinates that uncouple the equations of motion. The next step is to find how the normal coordinates and frequencies relate to the simulated vibrational motions and frequencies calculated for the anharmonic model system interacting, in this case, through the Morse potential functions defined in equation 1.

To relate the molecular vibrations of the harmonic system to the simulated vibrational trajectories of the model system, the students compare the harmonic frequencies to the frequencies calculated from the dominant peaks in the simulated Fourier spectrum. For the trajectory simulated in Figure 2, they find the normal frequencies correspond roughly to the frequencies of the two dominant peaks in the Fourier expansion illustrated in Figure 2d. Finally the dominant frequencies can be understood in terms of particular vibrational motions, those simple harmonic motions defined by the normal-mode analysis.

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In the last phase of this exercise, the students explore the limits of the normal mode description of vibration. This is accomplished by making classical simulations of the molecular motion using a variety of initial conditions.

When the vibrational dynamics simulation begins with a small (~ 0.01 Å) initial displacement of the atoms selected according to one of the normal-mode eigenvectors, the resulting motion appears simple and regular (see Figures 3a–d). In a truly harmonic system, energy does not flow from one normal mode to another. If only one normal mode is excited initially, the molecule continues to move according to the displacement vector of only that mode and the other normal mode(s) has no amplitude throughout the trajectory. In the present case, however, as in any realistic system, the harmonic expansion of the potential is only an approximation. For small enough displacements of the atoms from their equilibrium positions, it is a good approximation and the vibration of the molecule is well described by normal modes. Notice for this model the antisymmetric stretch in Figure 3c is approximated less well by a normal mode than the symmetric stretch in Figure 3a. It can be shown that a pure antisymmetric mode does not exist for the coupled-Morse potential model [16]. Even for very small displacements in the directions of the eigenvector for the antisymmetric stretch, some component of symmetric stretch mixes into the motion.

For larger displacements of the atoms, the higher-order terms in the Taylor approximation to the potential become more important and the harmonic approximation describes the system less well. Corrections to the harmonic approximation, called anharmonic corrections, couple the normal modes. A more complicated motion results, as evidenced by the trajectories in Figure 2a–c and the appearance of additional components in the frequency spectrum in Figure 2d. The shifting parabolic trajectory drawn in Figure 2b is characteristic of a system in which the antisymmetric vibrational mode oscillates at approximately twice the frequency of the symmetric mode, called 1-2 type vibrational resonance [16]. Furthermore, as the energy of the system increases causing larger atomic displacements, the frequency of vibration decreases in the coupled Morse oscillator. In contrast, the normal frequency is constant regardless of the atomic displacements in the harmonic system.

It is important to emphasize that the normal-mode analysis is just as valid in quantum mechanics as in classical mechanics. The difference is that each of the normal modes becomes a quantized harmonic oscillator with zero-point energy $\hbar\omega_k / 2$ and energy

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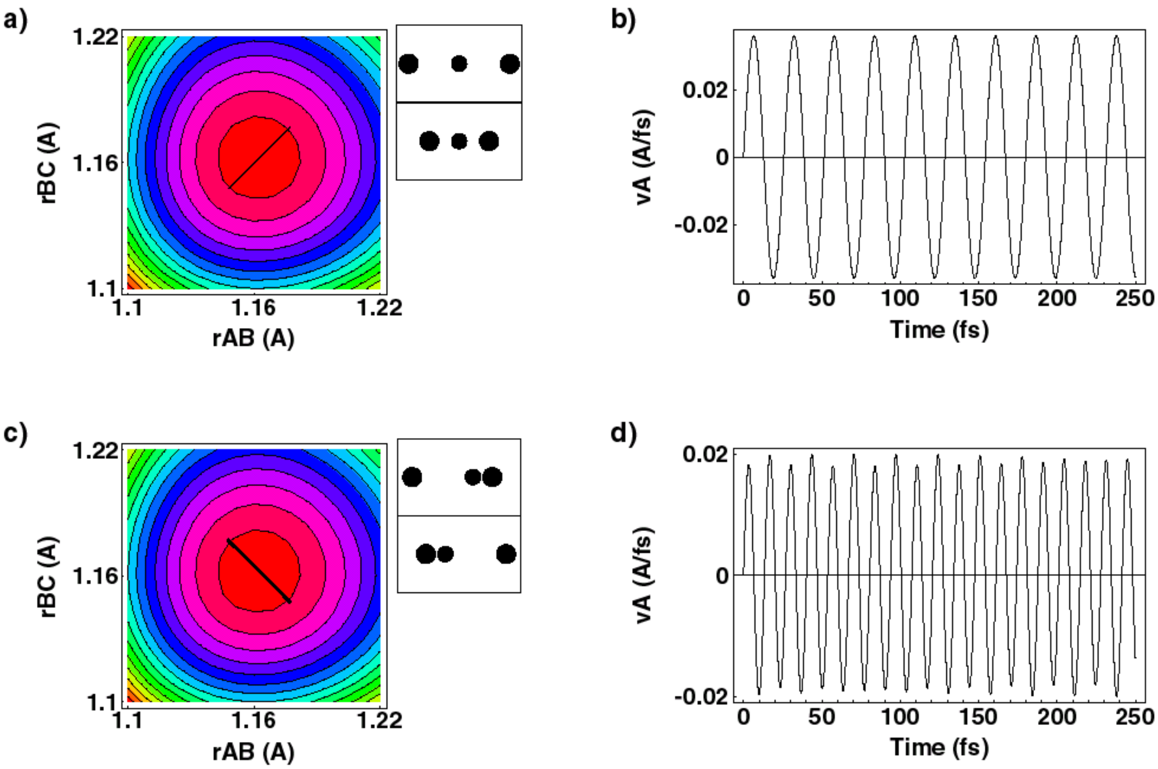

FIGURE 3. ILLUSTRATION AND ANALYSIS OF THE TIME EVOLUTION OF THE MOLECULE WHEN THE INITIAL CONDITIONS ARE CHOSEN TO MIMIC ONE OF THE TWO NORMAL MODES. (a) THE SYMMETRIC STRETCH WITH INITIAL DISPLACEMENTS IN ÅNGSTROMS: $x_A = -0.015$, $x_B = -0.28$, $x_C = 0.21$. TWO SNAPSHOTS OF THE MOLECULE FROM THE ANIMATION WINDOW APPEAR TO THE RIGHT OF THE CONTOUR PLOT. (b) THE VELOCITY OF ATOM A PLOTTED AS A FUNCTION OF TIME FOR THE TRAJECTORY SHOWN IN (a). (c) THE ANTISYMMETRIC STRETCH WITH INITIAL ATOMIC DISPLACEMENTS IN ÅNGSTROMS: $x_A = -0.005$, $x_B = 0.00$, $x_C = -0.015$. TWO SNAPSHOTS OF THE MOLECULE FROM THE ANIMATION WINDOW APPEAR TO THE RIGHT OF THE CONTOUR PLOT. (d) THE VELOCITY OF ATOM A PLOTTED AS A FUNCTION OF TIME FOR THE TRAJECTORY SHOWN IN (c).

levels separated by $\hbar\omega_k$, where k labels the normal mode. The frequency in the quantum problem, ω_k, is the same as the classical frequency of vibration found in the normal mode analysis.

Vibrations of Complex Molecules

Using the methods described above, the students can extend the calculation to study larger molecules in one dimension or even three dimensions. For a special project, a capable student can modify the simulation program to model 4 atoms, for example, and study such things as intramolecular vibrational energy transfer, the transition from normal- to local-mode-type behavior, and the onset of chaotic trajectories. Also, we have developed Mathematica programs for calculating and animating the normal modes of CO_2 and H_2O in three-dimensional space. The calculation requires the

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student to input bond lengths and spring constants. At the end of the exercise, if time permits, the students can run these program modules for different values of the input parameters and observe how the normal-mode frequencies change and how well they compare with spectroscopic data. Alternatively, the students can extend the existing codes to study vibrations in more complex molecules.

Conclusion

In the molecular-vibration exercise described here, the students study Morse and harmonic interaction potentials, perform molecular dynamics simulations of the atomic motion, resolve temporal information from atomic trajectories into frequency information by Fourier analysis, and finally calculate the normal modes and frequencies of vibration. In the process, the students have the opportunity to develop an understanding of potential interactions and different ways of describing them, the motivation for the normal-mode analysis, and the strengths and weaknesses of the normal-mode description of vibration. At the end of the exercise, the students should be better prepared for encounters with molecular vibration in their future work.

The exercise described in this article can be found on the Worldwide Web under http://www.chem.washington.edu/~chem465/Chem465Exercises, Exercise 4 [17].

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