

Molecular Vibrations

B. The harmonic approximation and normal modes

The amplitude of vibration at room temperature is quite small, on the order of 0.1 Angstrom or less. Therefore, the relevant region on the potential surface can, to a good approximation, be taken to be a harmonic oscillator potential. The harmonic approximation can be obtained by Taylor expanding the potential energy function about the minimum potential energy up to and including the second order term. Higher order corrections can then be added later with perturbation theory (so-called anharmonic corrections). Matlab can be used to carry out the Taylor expansion.

In this chapter we will use the same values for the potential parameters and mass as in part A.

```
-----  
% parameters.m  
  
bAB=1.162; % Equilibrium bond length in Angstrom  
bBC=1.162;  
  
alphaAB=2.5; % Decay length of Potnl. in 1/Angstrom  
alphaBC=2.5;  
  
dAB=7.65; % Potential well depth in eV <-> 61.717 1/cm  
dBC=7.65;  
  
mA=16.0; % Mass of O atom in atomic units  
mB=12.0; % Mass of C atom in atomic units  
mC=16.0; % Mass of O atom in atomic units  
-----
```

Then we define the potential function (a Morse potential for each bond, as in part A)

```
-----  
function y=potent(rAB,rBC)  
  
parameters  
  
potmorse1=dAB*(exp(-2*alphaAB*(rAB-bAB))-2*exp(-alphaAB*(rAB-bAB)));  
  
potmorse2=dBC*(exp(-2*alphaBB*(rAB-bBC))-2*exp(-alphaBC*(rAB-bBC)));  
  
y=ptmorse1+potmorse2;  
-----
```

The Taylor expansion can then be obtained with the taylor function. The function is expanded about the coordinates corresponding to the potential minimum, the most stable configuration of the atoms. In the Matlab command, one needs to create the symbolic variables rAB and rBC, give the function, the order of the highest term in the expansion plus one, the value of the variable at the expansion point and then the variable itself. Read the help file to learn more. The following m file creates a taylor expansion of the potential function. Notice that as the potential is a function of 2 variables, so the taylor command has to be used twice. The expansion here is about the point $r_{AB} = b_{AB}$ and $r_{BC} = b_{BC}$

```
-----
```

```

clear all
close all

parameters

syms rab rbc

f=potent(rab,rbc);

g=taylor(f,3,bAB,rab);

taylorpot=taylor(g,3,bBC,rbc);

pretty(taylorpot)
-----

```

Q1: Define a Matlab function giving the harmonic approximation to the Morse potential for the A-B interaction. Plot the harmonic potential function on top of a plot of the full Morse potential function (use different colors). Read from the graph the difference between the two functions at a vibrational amplitude that is typical of room temperature. Remember to give all constants in the potential function a numerical value before attempting to plot the function.

Q2: What is the spring constant, k_{AB} , of the A-B interaction in terms of the parameters for the A-B Morse potential? Differentiate by hand and then compare to the value that the Taylor expansion gave you.

Q3: Define a Matlab function giving the harmonic approximation to the full potential surface of the A-B-C molecule and plot a contour plot. Compare with the contour plot of the full potential surface (see part A). How does the shape of the contours compare in the two cases?

For harmonic potentials, the equation of motion is linear and the set of equations, one for each coordinate, can be solved as an eigenvalue problem. Assuming that a solution can be found where all the atoms in the molecule are moving with the same frequency, ω , that is, assuming that

$$\frac{d^2 x_A}{dt^2} = -\omega^2 x_A, \quad \frac{d^2 x_B}{dt^2} = -\omega^2 x_B \quad \text{and} \quad \frac{d^2 x_C}{dt^2} = -\omega^2 x_C,$$

the set of equations can be written as a matrix equation of the form

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

where k_{AB} is the spring constant for the AB bond and k_{BC} is the spring constant for the BC bond. This is an eigenvalue problem where the eigenvectors correspond to values $(\Delta x_A, \Delta x_B, \Delta x_C)$ and the eigenfrequencies give corresponding values of ω^2 . The eigenvalue problem can be solved easily in Matlab. First we give the spring constants a numerical value and then the matrix of coefficients needs to be defined.

```

EDU>> kAB=2*alphaAB^2*dAB;
EDU>> kBC=2*alphaBC^2*dBC;
EDU>> matrix=[kAB/mA -kAB/mA 0; -kAB/mB (kAB+kBC)/mB -kBC/mB; 0 -kBC/mC kBC/mC];

```

The eigenvectors and eigenvalues can then be found with the eig function (read the help file)

```

EDU>> [v,d]=eig(matrix)

```

The first output from Matlab is a matrix which has the eigenvalues (eigenfrequencies squared) on the main diagonal, then a matrix which has the eigenvectors for columns. The eigenvectors correspond to certain displacements of the atoms that are called 'normal modes' of vibration.

Q4: Describe in words the three solutions. Only two of them correspond to normal modes of vibration. What kind of motion do the three solutions correspond to? One of the normal modes is called 'symmetric stretch' and the other is called 'asymmetric stretch'. Which is which? What are the corresponding frequencies (since the unit of energy is eV, the unit of mass is amu, and the unit of length is Angstrom, the unit of time is ca. 10 fsec).

Q5: How does the frequency of the normal modes compare with the frequency corresponding to the dominant peaks in the Fourier expansion of the classical trajectory you calculated in part A? Compare with the values obtained from trajectories with both large as well as small initial displacements of the atoms. Which agree more closely with the normal mode frequencies (explain why)?

Q6: The normal mode analysis is just as valid in quantum mechanics as in classical mechanics. What would be the zero point energy of the A-B-C molecule, and what would be the excitation energy to the first excited vibrational state?

It is instructive to now go back to the classical dynamics simulation in part A and choose initial conditions in such a way as to excite only one of the normal modes.

Q7: Carry out classical dynamics calculations using the Matlab commands from part A, now choosing the initial conditions to excite only one of the normal modes. Plot the trajectory on top of the contour plot of the potential surface, and the position of atom A as a function of time. Do this for each of the two normal modes.

For small amplitude (ca. 0.05 Å and smaller), the normal modes are not coupled together because the harmonic approximation is a good approximation. This is particularly true for the symmetric stretch, but less so for the asymmetric stretch.

Q8: Can you rationalize the fact that the asymmetric stretch is less well described by the normal mode approximation by referring to the shape of the contours on the potential surface?

Q9: Change the masses and spring constants to represent a molecule where no two atoms are the same and calculate again the normal modes. Is there any symmetry (or antisymmetry) in the displacement of the atoms in the normal modes?