

Molecular Vibrations

In this set of exercises, you will study the vibration of molecules. The basic concepts will be illustrated with a simple example, a triatomic molecule confined to motion along a straight line. You will first of all carry out classical dynamics calculations using the velocity Verlet algorithm and observe the motion of the molecule by plotting the trajectories on top of the contour plot of the potential, as well as animation. By Fourier expanding the velocity of the atoms, you will then obtain the frequency spectrum for the vibrational motion. For comparison, you will calculate the normal modes of the vibrational motion by invoking the harmonic approximation and solving the equations of motion analytically. This turns out to be an eigenvalue problem where the vibrational frequency squared of each of the modes is a eigenvalue. The normal mode frequencies correspond approximately to the peaks in the frequency spectrum obtained from the calculated classical trajectories. It is very important that you carry out quantitative comparison of the results of the Fourier expansion and the normal mode analysis.

A. The frequency spectrum

The molecule consists of three atoms, A-B-C, which are confined to move along a straight line. Each of the two bonds are described by a Morse interaction potential

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

and

$$V_{BC}(r) = d_{BC} (e^{-2\alpha_{BC}(r-b_{BC})} - 2e^{-\alpha_{BC}(r-b_{BC})})$$

The total potential energy of the molecule is

$$V(r_{AB}, r_{BC}) = V_{AB}(r_{AB}) + V_{BC}(r_{BC})$$

First we define a Matlab function for the Morse potential.

```
-----  
function y=potMorse(r,d,alpha,b)  
y=d*(exp(-2*alpha*(r-b))-2*exp(-alpha*(r-b)));  
-----
```

Next choose parameters to roughly mimick a CO₂ molecule (the unit of energy is chosen to be eV, the unit of length is Angstrom, the unit of mass is amu, and the unit of time then ends up being approximately 10 fsec)

```
-----  
% 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;  
-----
```

It is a good idea to test and make sure the potential functions return numerical values, and then plot the functions. The parameter b gives the optimal bond length which should correspond to an energy of -d.

Evaluating the potMorse function for the AB bond at the distance bAB to test this

```
>> parameters
>> potMorse(bAB,dAB,alphaAB,bAB)
```

Then, plot the Morse potential

```
>> r=[0:0.01:3];
>> plot(r,potMorse(r,dAB,alphaAB,bAB))
>> axis([0 3 -10 20])
```

Q1: Read from the graph well depth and the optimal bond length. How do they relate to the potential parameters: d, b, and alpha?

Q2: The thermal energy at room temperature is $kT = 0.025$ eV, where k is the Boltzmann constant. Determine the amplitude of the vibrational motion at room temperature by reading off the plot of the Morse potential (find the classical turning points corresponding to an energy of kT . You will need to change the scale of the plot). What is the amplitude at 600 K?

Then, define a Matlab function for the full potential energy of the molecule, the sum of the Morse potentials for the two bonds

```
-----
function y=potent(rAB,rBC)

parameters % loads the values in parameters.m so potMorse can function

y=potMorse(rAB,dAB,alphaAB,bAB)+potMorse(rBC,dBC,alphaBC,bBC);
-----
```

Again, it is a good idea to evaluate the function at some point to make sure that the function returns a numerical result. We can, for example, evaluate the function at the optimal bond length for both bonds, $r_{AB}=b_{AB}$ and $r_{BC}=b_{BC}$

```
>> potent(bAB,bBC)
```

Q3: Is this value consistent with the value of the parameters dAB and dBC (explain your reasoning)?

Since there are only two independent variables in the problem, a contour plot can be used to illustrate the full potential energy surface

```
-----
% cntr.m

rABm=[0.8:0.05:2.6];
rBCm=[0.8:0.05:2.6];

[rABm,rBCm]=meshgrid(rABm,rBCm);

Z=potent(rABm,rBCm);

contourf(rABm,rBCm,Z,15); %Octave users:contour(rAB,rBC,Z,15);
caxis([-16 1]) % Remove if using Octave
xlabel('rAB')
ylabel('rBC')
-----
```

```
>> cntr
```

To find the force acting on each atom, we need to define 2 functions, dV/dr_{AB} and dV/dr_{BC} . There are 2

possible ways of doing this. The first is to make Matlab differentiate for you.

```
-----  
function y=dVdrAB(rAB,rBC)
```

```
syms r1d
```

```
difansw=diff(potent(r1d,rBC))
```

```
r1d=rAB;
```

```
y=subs(difansw);  
-----
```

and

```
-----  
function y=dVdrBC(rAB,rBC)
```

```
syms r1d
```

```
difansw=diff(potent(rAB,r1d));
```

```
r1d=rBC;
```

```
y=subs(difansw);  
-----
```

or use the derivative directly, as in

```
-----  
function y=dVdrAB(rAB,rBC)
```

```
parameters
```

```
y=dAB*(-2*alphaAB*exp(-2*alphaAB*(rAB-bAB))+2*alphaAB*exp(-alphaAB*(rAB-bAB)));  
-----
```

and

```
-----  
function y=dVdrBC(rAB,rBC)
```

```
parameters
```

```
y=dAB*(-2*alphaBC*exp(-2*alphaBC*(rBC-bBC))+2*alphaBC*exp(-alphaBC*(rBC-bBC)));  
-----
```

The velocity Verlet algorithm can be used to calculate the classical dynamics of the atoms in the molecule. It is simplest to work with a coordinate for each of the three atoms, $\{x_A, x_B, x_C\}$, even though there are only two independent variables in the problem. The distances between the molecules are denoted r_{AB} and r_{BC} . First, the time step size and total simulation time is specified and the number of time steps calculated. Then, the mass of the atoms is specified and the initial position and velocity of the atoms are specified. Finally, the velocity Verlet recursion equations are iterated for the required number of steps to map out the trajectory. This calculation will either take a short time or a very long time depending on which method you chose to use for dV/dr_{AB} and dV/dr_{BC} .

```
-----  
tic % Starts the stopwatch
```

```

h=0.04; % time step used in MD simulation
time=30.0; % 1 time unit = 10 fsec approximately
nsteps=round(time/h)+1;

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

xA(1)=-bAB-0.18; % xA=-bAB corresponds to optimal bond length if xB=0
xB(1)=0.00-0.28;
xC(1)=bBC+0.21; % xC=bBC corresponds to optimal bond length if xB=0

vA(1)=0.0; % Atomic velocity in Angstrom/10fsec
vB(1)=0.0;
vC(1)=0.0;

rAB(1)=xB(1)-xA(1); % Initial length of the A - B bond
rBC(1)=xC(1)-xB(1); % Initial length of the B - C bond

fA(1)=dVdrAB(rAB(1),rBC(1)); % Initial force on atom A
fB(1)=-dVdrAB(rAB(1),rBC(1))+dVdrBC(rAB(1),rBC(1));
fC(1)=-dVdrBC(rAB(1),rBC(1));

for n=1:nsteps-1

    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);
end

% Now create a table (matrix) with various information about the trajectory:
% coordinates, velocities, forces and energy

kin=(mA*vA.^2+mB*vB.^2+mC*vC.^2)/2;
pot=(potent(xB-xA,xC-xB));
energy=kin+pot;
trajdata=[xA',xB',xC',vA',vB',vC',fA',fB',fC',kin',pot',energy'];

toc % Stops the stopwatch and prints out the time the calculation took
-----

Be careful not to clear anything after completing this calculation. Now we can plot the trajectory in top of the
contour plot.

>> cntr

```

```
>> hold on
>> plot(rAB,rBC,'k')
```

Then, the motion of the atoms along the calculated trajectory can be animated

```
-----
hold off

nres=5;

% This loop picks out every fifth set of coordinates
for n=1:nres:nsteps
    ptA((n-1)/5+1)=xA(n);
    ptB((n-1)/5+1)=xB(n);
    ptC((n-1)/5+1)=xC(n);
end

nanimate=round(nsteps/nres);

for t=1:nanimate
    plot(ptA(t),0,'ob',ptB(t),0,'ok',ptC(t),0,'ob','MarkerSize',67)
    axis([-3 3 -3 3])
    axis off
    M(t) = getframe;
end

movie(M,5)
-----
```

Compare the animation with the plot of the trajectory on top of the contour plot. Note that the motion is asymmetric, the B-C distance has larger amplitude than the A-B distance, even though the bonds are equivalent. This is because of the molecule is initially distorted in an asymmetric way. The initial displacement of the bonds from the optimal length is quite large in this example.

Q4: How large is the initial bond length of the A-B bond and of the B-C bond in this example? (Look at the initial coordinates of the atoms).

Q5: Repeat the calculation and animation for slightly different initial displacements of the atoms, for example choose a nearly symmetric initial displacement (i.e. $r_{AB} = r_{BC}$). Note how sensitive the trajectory is to the initial geometry of the molecule.

Q6: Repeat the calculation and animation for initial displacements that are smaller, and more representative of room temperature, for example $x_A = -b_{AB} - 0.05$, $x_B = -0.10$, and $x_C = b_{BC} + 0.05$. Compare the plot of this trajectory (on top of the contour plot of the potential) with the ones you obtained before. What are the qualitative differences between the trajectory obtained with these small displacements and the one obtained with the large displacement you ran initially?

To obtain the frequency spectrum for the vibrational motion, you can Fourier expand the velocity of atom A, for example. (The coordinates could also be Fourier expanded giving peaks at the same frequencies, but since the coordinates oscillate about a non-zero value, a very large peak at zero frequency would then show up). Fourier expand by using the `fft` function in Matlab.

```
>> fur=abs(fft(vA));
```

The results can be plotted. This shows the magnitude of the amplitude of the various fourier components simply as a function of the number of the frequency component on the grid of frequency values.

```
>> plot(fur)
>> axis([0 100 0 90])
```

Note that the total number of frequency components that come out of the Fourier expansion is the same as

the number of points in the time series that is used as input. Before analysing the results of the Fourier expansion, it is important to recall the basic properties of the Fourier expansion. When a time series with points $t = \{0, h, 2h, 3h, \dots, Nh=T\}$ is Fourier expanded, a list of amplitudes corresponding to angular frequency $\omega = \{\omega_1, \omega_2, \omega_3, \dots, \omega_N\} = \{0, \Delta\omega, 2\Delta\omega, 3\Delta\omega, \dots, N\Delta\omega\}$ is returned. The smallest non-zero frequency corresponds to the term $\sin(2\pi t/T)$, so $\omega_2 = 2\pi/T$.

Q7: The difference in frequency between adjacent points in the Fourier expansion, $\Delta\omega$, is called the resolution. What determines the resolution (how could you improve the resolution)?

Q8: What is the largest frequency component that is included in the Fourier expansion? What determines the largest frequency component (how could you increase it)?

Q9: What are the frequencies (in inverse seconds) corresponding to the two dominant peaks in the frequency spectrum you obtained?

Q10: Determine the frequency corresponding to some of the smaller peaks. Is there a simple relationship between these frequencies and those of the two dominant peaks (hint: try sums and differences)?

Q11: Carry out the trajectory calculation again but run it only for half as long as before. Fourier expand and observe how the results change. How does the total length of the time series affect the results of the Fourier expansion?

Q12: Repeat the calculation of the trajectory and the Fourier expansion for even smaller displacements. Note how the frequency values corresponding to the two dominant peaks in the frequency spectrum changes slightly as the vibrational amplitudes are made smaller (this effect is due to anharmonicity in the potential surface).

Q13: Repeat the calculation of the trajectory displacing only atom A from the optimal position in the beginning, i.e. only stretching or compressing the A-B bond, leaving the B-C bond at the optimum length. Choose the mass of the end atoms to be much smaller than the central atom in this case (for example by a factor of 10). Note how, after certain amount of time, only the B-C bond is vibrating while the A-B bond is almost at rest (recall the demo in lecture with two penduli).