Computational Methods and Data Analysis 2003

Ex. 3: Dynamics of the O_2 molecule

We are there, in this exercise you are going to use Matlab to study a true physical system. By means of several algorithms for the integration of ODE's, you will follow the vibrational dynamics of two bonded oxigen atoms (O_2) interacting through a realistic potential. The results should be summarized in a report with text and figures. Do not forget to label the axis of each figure, possibly indicating the units. Describe the results and give in the text and/or in the captions all the values of the parameters which have been used in each calculation. The idea is that by reading the report and by using your programs, the reader should be able to reproduce the results.

Interatomic potential

The interatomic energies $V(r)$ as a function of the interatomic distances r of the O_2 molecule, calculated by the group of Theoretical Chemistry, are given in file `O2.txt`, which is located on the web site
`http:/www.theochem.kun.nl/~pwormer` clicking on the subject "Courses and teaching material" and then "Matlab lectures". Energies are given in Hartrees (1 Hartree = 2 Rydbergs = 2 × 13.6058 eV) for a discrete set of values of interatomic distances expressed in Bohr (1 Bohr = 5.29 10^{-11}m). You can load this text file in your matlab program and fit the data using the following interatomic potential (Morse potential):

$$V_M(r) = D_0 + D_1 \exp(-\beta r) + D_2 \exp(-2\beta r), \tag{1}$$

where r is the interatomic distance and D_0, D_1, D_2 and β are fitting parameters which you have to determine. In order to find them you start by determining D_0, D_1 and D_2 for different values of β (ranging for example from 0.1 to 3). Equating Eq. (1) to the exact values of the interactomic potential V leads to a system of n equations (where n is the number of points given in file `O2.txt`) with D_0, D_1 and D_2 as unknowns. This system can be recast in the form

$$A\mathbf{D} = \mathbf{V} \tag{2}$$

where $\mathbf{D}$ is a vector of dimension 3 ($D(1) = D_0$, $D(2) = D_1$ and $D(3) = D_2$), $\mathbf{V}$ is a vector of dimension n and A is the coefficient matrix (of dimension $n \times 3$). The solution of (2) is given by

$$\mathbf{D} = A^{-1}\mathbf{V} \tag{3}$$

The inverse of a matrix is performed by the backslash operator in Matlab:
`D = A \ V.`
In this way, for every fixed β, the values of D_0, D_1 and D_2 can be obtained. The optimal value of β is the one which minimizes the discrepancy between the fitted values **fit**$= A\mathbf{D}$ and the actual data $\mathbf{V}$, calculated in the following way

$$\text{norm}(\mathbf{V} - \mathbf{fit}) = \sqrt{\Sigma_{i=1}^{n}(V_i - fit_i)^2} \tag{4}$$

A possible Matlab code to perform the fit is given below:

```
load O2.txt;
r = O2(:,1);
V = O2(:,2);
clear O2;
n = length(r);
for i=1:300;
    beta=0.1+0.01*i;
  A = [ones(n,1), exp(-beta*r), exp(-2*beta*r)];
  D = A\V;
  fit = A*D;
  T(:,i)=[norm(V-fit)];
end
[Y,I]=min(T)
Beta=0.1+0.01*I
A = [ones(n,1), exp(-Beta*r), exp(-2*Beta*r)];
D = A\V
fit = A*D;
```

Plot the data and the calculated fit on the same graph, showing that indeed the potential V_M given in Eq. (1) is a good approximation. From the plot you can also find the position of the minimum of this potential either graphically or by use of the matlab function `fminsearch`. This minimum can also be calculated analytically. Differentiating Eq. (1) with respect to r one gets

$$\frac{dV}{dr} = -\beta D_1 \exp(-\beta r) - 2\beta D_2 \exp(-2\beta r). \tag{5}$$

The minimum is obtained when $\frac{dV}{dr} = 0$, which can be solved making the substitution $x = \exp(-\beta r)$:

$$2D_2 x^2 + D_1 x = 0,$$

which has (besides the solution for $x = 0$, i.e. $r = \infty$) the solution

$$x = x_{min} = -\frac{D_1}{2D_2}.$$

Thus the equilibrium interatomic distance is given by

$$r_{min} = -\frac{\ln x_{min}}{\beta} = \frac{\ln\left(-\frac{2D_2}{D_1}\right)}{\beta}. \tag{6}$$

Check that the minimum calculated by using Eq. (6) is in agreement with that determined graphically by plotting the data and by use of `fminsearch`.

Harmonic approximation

It is known from classical mechanics that every system characterized by a potential which has a stable equilibrium state can be described by means of a harmonic potential for small oscillations around the equilibrium. In fact if V(r) is a generic potential which has a local minimum for $r = r_{min}$ we can always perform an expansion for r close to r_{min} up to the second order:

$$V(r) \simeq V(r_{min}) + \frac{1}{2}\frac{d^2V}{dr^2}\Big|_{r=r_{min}}(r - r_{min})^2, \tag{7}$$

where we have used the fact that the linear term is zero since $\frac{dV}{dr}\Big|_{r=r_{min}} = 0$. Thus, using Eq. (7), we can approximate the full potential given in Eq. (1) by a harmonic one for small deviations from equilibrium. All we need is to calculate the second derivative. From Eq. (5)

$$\frac{d^2V}{dr^2} = \beta^2 D_1 \exp(-\beta r) + 4\beta^2 D_2 \exp(-2\beta r). \tag{8}$$

For $r = r_{min}$ we obtain, using the expression for r_{min} (Eq. (6))

$$K \equiv \frac{d^2V}{dr^2}\Big|_{r=r_{min}} = \beta^2 D_1 \left(-\frac{D_1}{2D_2}\right) + 4\beta^2 D_2 \left(-\frac{D_1}{2D_2}\right)^2 = \frac{\beta^2 D_1^2}{2D_2} \tag{9}$$

where we have defined the force constant K as the second derivative of the potential calculated at the minimum. In this way we can write the harmonic potential which approximates $V(r)$:

$$V^{harm}(r) = V(r_{min}) + \frac{1}{2}K(r - r_{min})^2. \tag{10}$$

Plot also $V^{harm}(r)$ and check that it approximates $V(r)$ in the vicinity of r_{min}.

Dynamics

Once you have fixed the form of the interatomic potential you can study the dynamics of the problem solving the equations of motion. However a complete anaytical solution can be only achieved for simple potentials, such as the harmonic potential. In general you have to solve the problem by integrating the equations of motion numerically. Suppose that our O_2 molecule can only move in one dimension. Denote the coordinates of the oxygen atoms respectively by x_1 and x_2. The interatomic potential is thus

$$V(x_1, x_2) = D_0 + D_1 \exp(-\beta(x_2 - x_1)) + D_2 \exp(-2\beta(x_2 - x_1))$$

($r = x_2 - x_1$) and the equations of motion are

$$\begin{cases} m\ddot{x}_1 &= -\frac{\partial V}{\partial x_1} \\ m\ddot{x}_2 &= -\frac{\partial V}{\partial x_2} \end{cases} \tag{11}$$

where m is the oxygen mass (16 a.u.). The right-hand side of these equations can be easily calculated:

$$-\frac{\partial V}{\partial x_1} = -\frac{dV}{dr}\frac{\partial r}{\partial x_1} = -\beta(D_1 \exp(-\beta(x_2 - x_1)) + 2D_2 \exp(-2\beta(x_2 - x_1))) \tag{12}$$

$$-\frac{\partial V}{\partial x_2} = -\frac{dV}{dr}\frac{\partial r}{\partial x_2} = \beta(D_1 \exp(-\beta(x_2 - x_1)) + 2D_2 \exp(-2\beta(x_2 - x_1))) \tag{13}$$

As expected, $\frac{\partial V}{\partial x_1} = -\frac{\partial V}{\partial x_2}$. In this way the equations of motion are

$$\begin{cases} m\ddot{x}_1 &= -\beta(D_1 \exp(-\beta(x_2 - x_1)) + 2D_2 \exp(-2\beta(x_2 - x_1))) \\ m\ddot{x}_2 &= \beta(D_1 \exp(-\beta(x_2 - x_1)) + 2D_2 \exp(-2\beta(x_2 - x_1))) \end{cases} \tag{14}$$

Initial conditions

Consider the following initial conditions:

$$x_1 = -\frac{1}{2}(r_{min} + \epsilon), \qquad x_2 = \frac{1}{2}(r_{min} + \epsilon)$$

$$\dot{x}_1 = 0, \qquad \dot{x}_2 = 0$$

for a few values of ϵ (for instance $|\epsilon|$ up to 0.3).

Numerical solution

Several methods can be used to solve a system of ordinary differential equations. For example, Matlab has a built-in routine, called ODE45, which uses the fourth-order Runge-Kutta method with adaptive step size. The routine requires as input a parameter (tolerance) which gives the accuracy of the result. Set it to 10^{-5}. We will consider this the exact solution of the problem and will use it for comparison while using the other methods. To use ODE45 the original system of ordinary differential equations has to be written as a system of first order differential equations. This can be easily done by making the substitutions

$$\begin{cases} y_1 &= x_1 \\ y_2 &= \dot{x}_1 \\ y_3 &= x_2 \\ y_4 &= \dot{x}_2 \end{cases} \tag{15}$$

Thus, Eq. (14) becomes

$$\begin{cases} \dot{y}_1 &= y_2 \\ \dot{y}_2 &= -\beta(D_1 \exp(-\beta(y_3 - y_1)) + 2D_2 \exp(-2\beta(y_3 - y_1)))/m \\ \dot{y}_3 &= y_4 \\ \dot{y}_4 &= \beta(D_1 \exp(-\beta(y_3 - y_1)) + 2D_2 \exp(-2\beta(y_3 - y_1)))/m \end{cases} \tag{16}$$

Note that the integration time should be much larger than one oscillation period. Besides this built-in Matlab routine you can write your own code to solve Eq. (14). We suggest four alternative methods.

Euler

This method can be applied to a system of first order ordinary differential equations of the type

$$\frac{dy_i(t)}{dt} = f_i(y_1(t), y_2(t), ..., y_n(t); t), \qquad i = 1, ..., n \tag{17}$$

($n = 4$ in Eq. (16)). Then, the solution at time $t + h$, where h is the time step, is given according to the Euler method by

$$y_i(t + h) = y_i(t) + hf_i(y_1(t), y_2(t), ..., y_n(t); t) + O(h^2) \tag{18}$$

Note that in our problem the f_i do not explicitly depend on time.

Improved Euler

The Euler method is not very accurate and not very stable, since positions and velocities are determined with an error $O(h^2)$. This method can be improved by considering the next order in the Taylor expansion of the solution:

$$y_i(t+h) = y_i(t)+hf_i(y_1(t), y_2(t), ..., y_n(t); t)+\frac{h^2}{2}\frac{df_i(y_1(t), y_2(t), ..., y_n(t); t)}{dt}+O(h^3) \quad (19)$$

. Using the notation

$$k_i^{(1)} = f_i(y_1(t), ..., y_n(t); t)$$
$$k_i^{(2)} = f_i\left(y_1(t) + hk_1^{(1)}, ..., y_n(t) + hk_n^{(1)}; t + h\right)$$

the solution can be written as

$$y_i(t+h) = y_i(t) + \frac{h}{2}(k_i^{(1)} + k_i^{(2)}) + O(h^3) \quad (20)$$

The error is now $O(h^3)$.

Runge-Kutta 4

One can obtain even more accurate solutions by using the Runge-Kutta method. Here the solution at time $t+h$ is given by

$$y_i(t+h) = y_i(t) + h\left(\frac{k_i^{(1)}}{6} + \frac{k_i^{(2)}}{3} + \frac{k_i^{(3)}}{3} + \frac{k_i^{(4)}}{6}\right) + O(h^5) \quad (21)$$

where $k_i^{(1)}$, $k_i^{(2)}$, $k_i^{(3)}$ and $k_i^{(4)}$ are defined as

$$k_i^{(1)} = f_i(y_1(t), ..., y_n(t); t)$$
$$k_i^{(2)} = f_i\left(y_1(t) + \frac{h}{2}k_1^{(1)}, ..., y_n(t) + \frac{h}{2}k_n^{(1)}; t + \frac{h}{2}\right)$$
$$k_i^{(3)} = f_i\left(y_1(t) + \frac{h}{2}k_1^{(2)}, ..., y_n(t) + \frac{h}{2}k_n^{(2)}; t + \frac{h}{2}\right)$$
$$k_i^{(4)} = f_i\left(y_1(t) + hk_1^{(3)}, ..., y_n(t) + hk_n^{(3)}; t + h\right)$$

Velocity Verlet

In this case we can start directly from the equations of motion, without needing to convert the original system into a system of first order differential equations. For one particle we have

$$\left\{\begin{array}{rcl} \frac{d\mathbf{r}}{dt} & = & \mathbf{v}(t) \\ \frac{d^2\mathbf{r}}{dt^2} & = & \mathbf{a}(\mathbf{r}) \end{array}\right. \quad (22)$$

The solution in the velocity Verlet scheme is

$$\left\{\begin{array}{rcl} \mathbf{r}(t+h) & = & \mathbf{r}(t) + h\mathbf{v}(t) + \frac{1}{2}h^2\mathbf{a}(t) + O(h^4) \\ \mathbf{v}(t+h) & = & \mathbf{v}(t) + \frac{h}{2}(\mathbf{a}(t) + \mathbf{a}(t+h)) + O(h^2) \end{array}\right. \quad (23)$$

The generalization to more than one particle is straightforward.

Plot the positions and velocities of both particles as a function of time comparing the solutions of the five proposed methods. Check that the accuracy of the solutions given by the Euler and improved methods is indeed worst than that of the other methods. Comment on the values of the used time steps.

Comparison to harmonic motion

It is interesting to study up to which deviations from equilibrium the motion can be described as harmonic. Solve the equations of motion for the harmonic potential problem

$$\left\{\begin{array}{rcl} m\ddot{x}_1 & = & K(x_2 - x_1 - r_{min}) \\ m\ddot{x}_2 & = & -K(x_2 - x_1 - r_{min}) \end{array}\right. \tag{24}$$

either numerically or analytically and compare the results for the relative motion to the one resulting from $V(r)$ for several values of the deviation from equilibrium ϵ. Note that in order to obtain the analytical solution of Eq. (24) it is convenient to solve the equation for $r = x_2 - x_1$. In the limit in which the harmonic approximation is valid, calculate the period of oscillations in seconds.