Mathematics, Data & Molecular Modelling
(Handout on the Verlet Method)

1 Hamiltonian Systems

In molecular dynamics, as well as in other fields such as celestial mechanics and classical mechanics, solutions are sought for the *Hamiltonian* system of ordinary differential equations (ODEs):

$$\begin{cases} \dot{p} = -\frac{\partial H}{\partial q}(p,q), \\ \dot{q} = \quad \frac{\partial H}{\partial p}(p,q), \end{cases} \tag{1}$$

where

$$H(p_1, \ldots, p_d, q_1, \ldots, q_d)$$

denotes the total energy (the *Hamiltonian*) of the system. The variables q_i and p_i represent the position coordinates and the corresponding momenta, respectively. The integer d denotes the number of degrees of freedom of the system.

Exercise D1

Consider the one-dimensional case $d = 1$, that is, $H = H(p, q)$.

Using the chain rule (see the first lecture), show that the energy remains constant along solutions of the system:

$$H(p(t), q(t)) = \textit{constant}.$$

Hint: *Compute the derivative*

$$\frac{dH}{dt}.$$

The Mathematical Pendulum

The undamped mathematical pendulum (see Figure 1) with mass $m = 1$, a massless string of length $l = 1$, and gravitational acceleration $g = 1$ (i.e. normalized values) is a system with one degree of freedom.

The variable q now represents the angle that the pendulum makes with the axis in the direction of gravity. The corresponding Hamiltonian is

$$H(p,q) = \frac{1}{2}p^2 - \cos(q), \tag{2}$$

so that the equations of motion (1) become (with now $p = y$ and $q = x$):

$$\begin{cases} \dot{x} = y, \\ \dot{y} = -\sin(x). \end{cases} \tag{3}$$

Thus, $y = \dot{x}$ represents the velocity.
Note that in a more general situation the equation becomes

$$m\ddot{q} = -\frac{g}{l}\sin(q),$$

which follows from the relation "$F = m \times a$".

Exercise D2

Show that for small displacements (small angles) x, the equations of motion of the pendulum simplify to

$$\dot{x} = y, \qquad \dot{y} = -x.$$

Verify that, for the initial conditions

$$x(0) = 1, \qquad y(0) = 0,$$

the solution is given by

$$x(t) = \cos(t), \qquad y(t) = -\sin(t).$$

What does the solution curve look like in the x-y plane? (Use the time t as a parameter for the curve.)

Also find an expression for the energy H for the approximated ("small angle") case.

Another example is given by two mutually attracting bodies (such as the Earth and the Moon). These bodies obey Newton's laws of mechanics and have the following Hamiltonian:

$$H(p_1,p_2,q_1,q_2) = \frac{1}{2}(p_1^2 + p_2^2) - \frac{1}{\sqrt{q_1^2 + q_2^2}}.$$

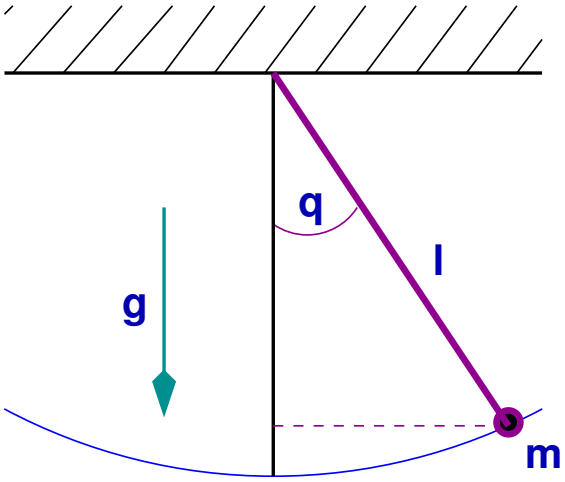


Figure 1: The mathematical pendulum.

Exercise D3

Derive the equations of motion for this system.
Hint: *Use equations (1).*

2 Some Basic Numerical Methods

Consider the system of ODEs

$$\begin{cases} \dot{x} = a(x, y), \\ \dot{y} = b(x, y), \end{cases} \tag{4}$$

for given functions a and b.

The simplest of all numerical methods for ordinary differential equations is Euler Forward (EF; see Chapter 19.1 of Kreyszig), named after Leonhard Euler (see Figure 2). For system (4), it is given by

$$\begin{cases} x^{n+1} = x^n + \Delta t\, a(x^n, y^n), \\ y^{n+1} = y^n + \Delta t\, b(x^n, y^n). \end{cases} \tag{5}$$

Here, Δt is the constant time step used to advance from time t^n to time t^{n+1}:

$$\Delta t = t^{n+1} - t^n.$$

This is an *explicit* method; this means that at every time level t^n the "new" solution follows directly from the "old" solution (i.e. the solution at the previous time level).

An example of an *implicit* method is Euler Backward (EB). Applying this method to system (4) gives

$$\begin{cases} x^{n+1} = x^n + \Delta t\, a(x^{n+1}, y^{n+1}), \\ y^{n+1} = y^n + \Delta t\, b(x^{n+1}, y^{n+1}). \end{cases} \tag{6}$$

As can be seen, at every time step a system of equations has to be solved in order to obtain x^{n+1} from x^n (and similarly y^{n+1} from y^n).
A method that uses a combination of EF and EB is called a partitioned Euler method. In this particular case it is referred to as *symplectic Euler* (SY):

$$\begin{cases} x^{n+1} = x^n + \Delta t\, a(x^{n+1}, y^n), \\ y^{n+1} = y^n + \Delta t\, b(x^{n+1}, y^n). \end{cases} \tag{7}$$

If we apply these three methods to the simplified system from Exercise D2, we immediately observe several different effects. These are shown in Figures 3 and 4 (with step size $\Delta t = 0.1$ and final time $T = 2\pi$).

A remarkable feature is the behavior of the energy

$$H = x^2 + y^2$$

as a function of time t. This quantity should remain constant. However, for EF we observe an increase in the energy (the solution curves form outward spirals instead of circles), while for EB the energy decreases (the solution curves form inward spirals). For SY, the numerical solution follows the periodic orbit reasonably well (at least visually), and moreover the energy remains close to the constant exact value 1.

The numerical error of these three methods is of order

$$\mathcal{O}(\Delta t).$$

This can be derived using Taylor expansions. It means that if the step size is reduced by a factor of 2, the numerical error will also decrease by approximately a factor of 2.

The fourth method shown in Figures 3 and 4 ('Verlet') will be discussed next.



Figure 2: Leonhard Euler (1707–1783).

3 The Verlet Method

In molecular dynamics, Hamiltonian systems are often used, where the total energy is given by

$$H(p,q) = \frac{1}{2}\sum_{i=1}^{N}\frac{1}{m_i}p_i^T p_i + \sum_{i=2}^{N}\sum_{j=1}^{i-1} V_{ij}(\parallel q_i - q_j \parallel), \tag{8}$$

with V_{ij} given potential functions.

In this case, the variables q_i and p_i represent the positions and momenta of the atoms, respectively, and m_i denotes the atomic mass of the i-th atom.

Note that in celestial mechanics a similar system also exists for a model describing the trajectories of the Earth and the other planets around the Sun (the N-body problem), with

$$V_{ij} = -G\frac{m_i m_j}{r}.$$

In molecular dynamics, the Lennard–Jones potential is frequently used:

$$V_{ij} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]. \tag{9}$$

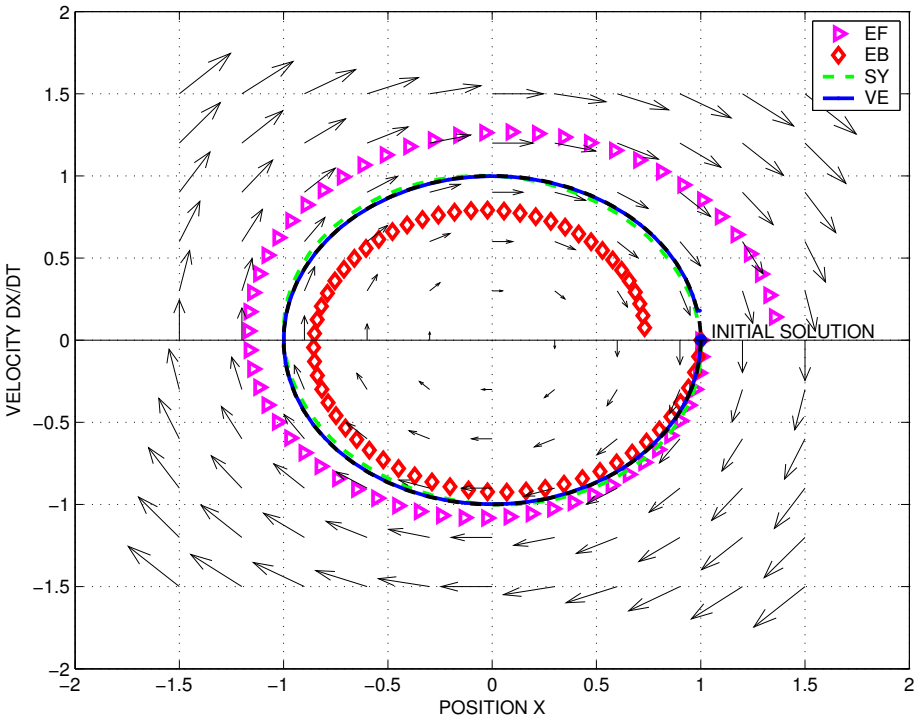


Figure 3: Numerical results for EF, EB, SY, and Verlet for the simplified pendulum equation (in the phase plane x-y).

Here, ϵ_{ij} and σ_{ij} are suitable constants that depend on the specific atoms involved.

The Hamiltonian (total energy) H in (8) can be written in the form

$$H(p,q) = T(p) + U(q),$$

where $T(p)$ is a quadratic function (because it contains terms of the form p_i^2).

The corresponding Hamiltonian system (1) then becomes in this case

$$\begin{cases} \dot{q} = M^{-1}p, \\ \dot{p} = -\nabla U(q). \end{cases}$$

Here, M is the matrix

$$M = \mathrm{diag}(m_1 I, \ldots, m_N I),$$

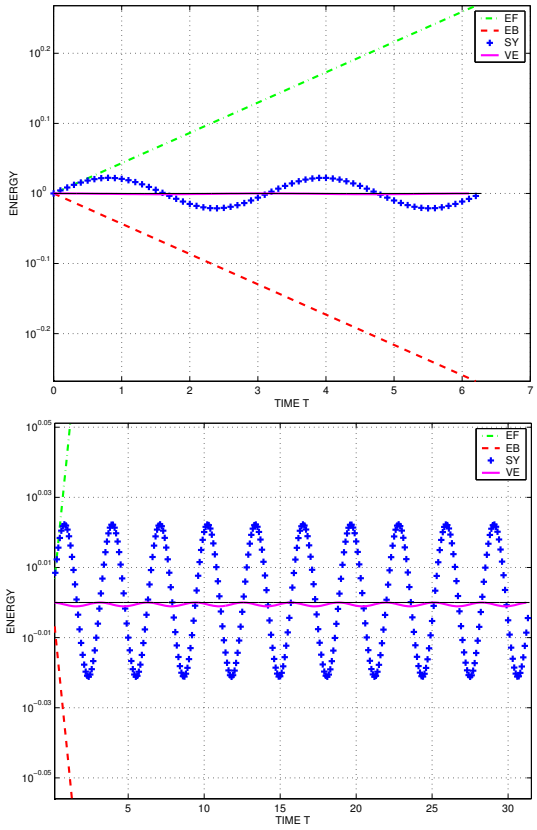


Figure 4: Numerical results for EF, EB, SY, and Verlet for the simplified pendulum equation; the energy H as a function of time t. Bottom: zoomed-in view; the y-axis is plotted on a logarithmic scale.

where I is the three-dimensional identity matrix, and

$$\nabla U = \frac{\partial U}{\partial q}$$

denotes the gradient of U.
This system is equivalent to the second-order differential equation

$$\ddot{q} = f(q), \tag{10}$$

where the right-hand side

$$f(q) = -M^{-1}\nabla U(q)$$

does not depend on $\dot{q}$.

A straightforward numerical approximation of equation (10) is

$$q^{n+1} - 2q^n + q^{n-1} = (\Delta t)^2 f(q^n). \tag{11}$$

Exercise D4

Using a Taylor expansion, show that

$$\ddot{q}(t^n) = \frac{q^{n+1} - 2q^n + q^{n-1}}{(\Delta t)^2} + F_1,$$

where the first term in the numerical error F_1 is given by

$$-\frac{1}{12}(\Delta t)^2 \frac{d^4 q}{dt^4}.$$

Exercise D5

Consider the system in exercise D2. Write the numerical value of the energy $(x^{n+1})^2 + (y^{n+1})^2$ at time t^{n+1} as a function of the energy at time t^n. Do this for EF, EB and the 'implicit midpoint method':

$$\begin{cases} x^{n+1} = x^n + \frac{\Delta t}{2}\ (y^n + y^{n+1}), \\ y^{n+1} = y^n - \frac{\Delta t}{2}\ (x^n + x^{n+1}). \end{cases} \tag{12}$$

Does the 'numerical energy' decrease, increase, or remain (approximately) constant?

The Verlet method is a second-order method, i.e. the numerical error is of order $(\Delta t)^2$ (halving the step size Δt gives approximately a factor 4 reduction in the error). This can be clearly seen in Figures 3 and 4. The trajectory of the numerical curve almost coincides with the exact solution (the circle), and the error in the energy is many times smaller than that for the other three methods.



Figure 5: Fredrik C. Mülertz Størmer (1874-1957) & Loup Verlet (1931-2019).