# 4

# Molecular dynamics

## 4.1 Basic integration schemes

### 4.1.1 General concepts

- Aim of Molecular Dynamics (MD) simulations:
  compute *equilibrium* and *transport* properties of *classical many body systems*.
- Basic strategy: numerically solve equations of motions.
- For many classical systems, the equations of motion are of Newtonian form

$$\dot{R}^N = \frac{1}{m} P^N$$
$$\dot{P}^N = F^N = -\frac{\partial U}{\partial R^N},$$

  or

$$\dot{X}^N = \mathcal{L} X^N, \text{ with } \mathcal{L}A = \{A, \mathcal{H}\},$$

  where $X^N = (R^N, P^N)$.
  The energy $\mathcal{H} = \frac{P^N \cdot P^N}{2m} + U(R^N)$ is conserved under this dynamics.
  The potential energy is typically of the form of a sum of pair potentials:

$$U(R^N) = \sum_{(i,j)} \varphi(r_{ij}) = \sum_{i=1}^{N} \sum_{j=1}^{i-1} \varphi(r_{ij}),$$

  which entails the following expression for the forces $F^N$:

$$\mathbf{F}_i = -\sum_{j \neq i} \frac{\partial}{\partial \mathbf{r}_i} \varphi(r_{ij}) = -\sum_{j \neq i} \varphi'(r_{ij}) \frac{\partial r_{ij}}{\partial \mathbf{r}_i} = \sum_{j \neq i} \underbrace{\varphi'(r_{ij}) \frac{\mathbf{r}_j - \mathbf{r}_i}{r_{ij}}}_{\mathbf{F}_{ij}}$$

- Examples of quantities of interest:

  1. Radial distribution function (structural equilibrium property)

$$g(r) = \frac{2V}{N(N-1)} \sum_{(i,j)} \langle \delta(\mathbf{r}_i - \mathbf{r}_j - \mathbf{r}) \rangle \,,$$

  where

$$\langle A \rangle = \frac{\int dX^N \; A(X^N) e^{-\beta \mathcal{H}(X^N)}}{\int dX^N \; e^{-\beta \mathcal{H}(X^N)}} \qquad \text{(canonical ensemble)}$$

$$\text{or} \quad = \frac{\int dX^N \; A(X^N) \; \delta(E - \mathcal{H}(X^N))}{\int dX^N \; \delta(E - \mathcal{H}(X^N))} \qquad \text{(microcanonical ensemble).}$$

  2. Pressure (thermodynamic equilibrium property):

$$pV = NkT + \frac{1}{3} \sum_{(i,j)} \langle \mathbf{F}_{ij} \cdot \mathbf{r}_{ij} \rangle$$

  which can be written in terms of $g(r)$ as well.

  3. Mean square displacement (transport property):

$$\left\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \right\rangle \to 6Dt \text{ for long times } t,$$

  where $D$ is the self diffusion coefficient.

  4. Time correlation function (relaxation properties)

$$C(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$$

  which is related to $D$ as well:

$$D = \frac{1}{3} \lim_{t \to \infty} \lim_{N,V \to \infty} \int_0^t C(\tau) \, d\tau$$

- If the system is ergodic then time average equals the microcanonical average:

$$\lim_{t_{\text{final}} \to \infty} \frac{1}{t_{\text{final}}} \int_0^{t_{\text{final}}} dt \; A(X^N(t)) = \frac{\int dX^N \; A(X^N) \; \delta(E - \mathcal{H}(X^N))}{\int dX^N \; \delta(E - \mathcal{H}(X^N))}.$$

- For large $N$, microcanonical and canonical averages are equal for many quantities $A$.

- Need long times $t_{\text{final}}$!

- The equations of motion to be solved are ordinary differential equations.
- There exist general algorithms to solve ordinary differential equations numerically (see e.g. *Numerical Recipes* Ch. 16), such as Runge-Kutta and predictor/correction algorithms. Many of these are too costly or not stable enough for long simulations of many-particle systems. In MD simulations, it is therefore better to use algorithms specifically suited for systems obeying Newton's equations of motion, such as the Verlet algorithm.
- However, we first want to explore some general properties of integration algorithms. For this purpose, consider a function $x$ of $t$ which satisfies

$$\dot{x} = f(x,t). \tag{4.1}$$

- We want to solve for the trajectory $x(t)$ numerically, given the initial point $x(0)$ at time $t = 0$.
- Similar to the case of integration, we restrict ourselves to a discrete set of points, separated by a *small time step* $\Delta t$:

$$t_n = n\Delta t$$
$$x_n = x(t_n),$$

  where $n = 0, 1, 2, 3, \ldots$.
- To transform equation (4.1) into a closed set of equations for the $x_n$, we need to express the time derivative $\dot{x}$ in terms of the $x_n$. This can only be done approximately.
- Using that $\Delta t$ is small:

$$\dot{x}(t_n) \approx \frac{x(t_n + \Delta t) - x(t_n)}{\Delta t} = \frac{x_{n+1} - x_n}{\Delta t}.$$

- Since this should be equal to $f(x(t), t) = f(x_n, t_n)$:

$$\frac{x_{n+1} - x_n}{\Delta t} \approx f(x_n, t_n) \Rightarrow$$
$$\boxed{x_{n+1} = x_n + f(x_n, t_n)\Delta t} \quad \textit{Euler Scheme}. \tag{4.2}$$

  This formula allows one to generate a time series of points which are an approximation to the real trajectory. A simple MD algorithm in pseudo-code could look like this:[1]

[1] Pseudo-code is an informal description of an algorithm using common control elements found in most programming language and natural language; it has no exact definition but is intended to make implementation in a high-level programming language straightforward.

```
EULER ALGORITHM
SET x to the initial value x(0)
SET t to the initial time
WHILE t < tfinal
   COMPUTE f(x,t)
   UPDATE x to x+f(x,t)*dt
   UPDATE t to t+dt
END WHILE
```

DO NOT USE THIS ALGORITHM!

- It is easy to show that the error in the Euler scheme is of order $\Delta t^2$, since

$$x(t+\Delta t) = x(t) + f(x(t),t)\Delta t + \frac{1}{2}\ddot{x}(t)\Delta t^2 + \ldots,$$

so that

$$x_{n+1} = x_n + f(x_n,t_n)\Delta t + \underbrace{\mathcal{O}(\Delta t^2)}_{\text{local error}}. \tag{4.3}$$

The strict meaning of the "big O" notation is that if $A = \mathcal{O}(\Delta t^k)$ then $\lim_{\Delta t\to 0} A/\Delta t^k$ is finite and nonzero. For small enough $\Delta t$, a term $\mathcal{O}(\Delta t^{k+1})$ becomes smaller than a term $\mathcal{O}(\Delta t^k)$, but the big O notation cannot tell us what magnitude of $\Delta t$ is small enough.

- A numerical prescription such as (4.3) is called an *integration algorithm*, *integration scheme*, or *integrator*.

- Equation (4.3) expresses the error after one time step; this is called the *local truncation error*.

- What is more relevant is the *global error* that results after a given physical time $t_f$ of order one. This time requires $M = t_f/\Delta t$ MD steps to be taken.

- Denoting $f_k = f(x_k,t_k)$, we can track the errors of subsequent time steps as follows:

$$\begin{aligned}
x_1 &= x_0 + f_0\Delta t + \mathcal{O}(\Delta t^2)\\
x_2 &= [x_0 + f_0\Delta t + \mathcal{O}(\Delta t^2)] + f_1\Delta t + \mathcal{O}(\Delta t^2)\\
&= x_0 + (f_0+f_1)\Delta t + \mathcal{O}(\Delta t^2) + \mathcal{O}(\Delta t^2)\\
&\vdots\\
x_M &= x_0 + \sum_{k=1}^{M} f_{k-1}\Delta t + \sum_{k=1}^{M}\mathcal{O}(\Delta t^2);
\end{aligned}$$

but as $M = t_f/\Delta t$:

$$x(t) = x_M = x_0 + \sum_{k=1}^{t_f/\Delta t} f_{k-1}\Delta t + \underbrace{\sum_{k=1}^{t_f/\Delta t} \mathcal{O}(\Delta t^2)}_{\text{global error}}.$$

- Since $t_f = \mathcal{O}(1)$, the accumulated error is

$$\sum_{k=1}^{t_f/\Delta t} \mathcal{O}(\Delta t^2) = \mathcal{O}(\Delta t^2)\mathcal{O}(t_f/\Delta t) = \mathcal{O}(t_f \Delta t), \tag{4.4}$$

  which is of first order in the time step $\Delta t$.

- Since the global error goes as the first power of the time step $\Delta t$, we call equation (4.3) a *first order* integrator.

- In absence of further information on the error terms, this constitutes a general principle: If in a single time step of an integration scheme, the local truncation error is $\mathcal{O}(\Delta t^{k+1})$, then the globally accumulated error over a time $t_f$ is $\mathcal{O}(t_f \Delta t^k) = \mathcal{O}(\Delta t^k)$, i.e., the scheme is $k$th order.

- Equation (4.4) also shows the possibility that the error grows with physical time $t_f$: *Drift*.

- Illustration of local and global errors:
  Let $f(x,t) = -\alpha x$, so that equation (4.1) reads

$$\dot{x} = -\alpha x,$$

  whose solution is exponentially decreasing with a rate $\alpha$:

$$x(t) = e^{-\alpha t} x(0). \tag{4.5}$$

  The numerical scheme (4.3) gives for this system

$$x_{n+1} = x_n - \alpha x_n \Delta t. \tag{4.6}$$

  Note that the true relation is $x(t+\Delta t) = e^{-\alpha \Delta t} x(t) = x(t) - \alpha \Delta t x(t) + \mathcal{O}(\Delta t^2)$, i.e., the local error is of order $\Delta t^2$.

  Equation (4.6) is solved by

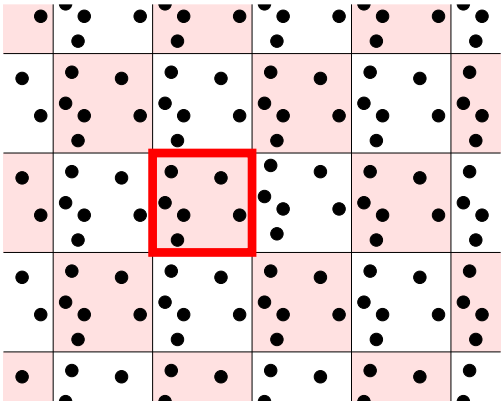
$$x_n = (1 - \alpha \Delta t)^n x_0 = (1 - \alpha \Delta t)^{t/\Delta t} = e^{[\ln(1-\alpha\Delta t)/\Delta t]t}. \tag{4.7}$$

By comparing equations (4.5) and (4.7), we see that the behaviour of the numerical solution is similar to that of the real solution but with the rate $\alpha$ replaced by $\alpha' = -\ln(1-\alpha\Delta t)/\Delta t$. For small $\Delta t$, one gets for the numerical rate $\alpha' = \alpha+\alpha^2\Delta t/2+\cdots = \alpha+\mathcal{O}(\Delta t)$, thus the global error is seen to be $\mathcal{O}(\Delta t)$, which demonstrates that the Euler scheme is a first order integrator. Note that the numerical rate diverges at $\Delta t = 1/\alpha$, which is an example of a numerical instability.

### 4.1.2 Ingredients of a molecular dynamics simulation

1. *Boundary conditions*

   - We can only simulate finite systems.
   - A wall potential would give finite size effects and destroy translation invariance.
   - More benign boundary conditions: *Periodic Boundary Conditions:*
   - Let all particles lie in a simulation box with coordinates between $-L/2$ and $L/2$.
   - A particle which exits the simulation box, is put back at the other end.
   - Infinite checkerboard picture (easiest to visualize in two dimensions):



   - The box with thick boundaries is our simulation box.
   - All other boxes are copies of the simulation box, called periodic images.
   - The other squares contain particles with shifted positions

$$\mathbf{r}' = \mathbf{r} + \begin{pmatrix} iL \\ jL \\ kL \end{pmatrix},$$

   for any negative or positive integers $i$, $j$, and $k$. Thus, if a particle moves out of the simulation box, another particle will fly in from the other side.

Conversely, for any particle at position $\mathbf{r}'$ not in the simulation box, there is a particle in the simulation box at

$$\mathbf{r} = \begin{pmatrix} (x' + \frac{L}{2}) \bmod L - \frac{L}{2} \\ (y' + \frac{L}{2}) \bmod L - \frac{L}{2} \\ (z' + \frac{L}{2}) \bmod L - \frac{L}{2} \end{pmatrix}, \tag{4.8}$$

- Yet another way to view this is to say that the system lives on a torus.

2. *Forces*

   - Usually based on pair potentials.
   - A common pair potential is the Lennard-Jones potential

     $$\varphi(r) = 4\varepsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right],$$

     - $\sigma$ is a measure of the range of the potential.
     - $\varepsilon$ is its strength.
     - The potential is positive for small $r$: repulsion.
     - The potential is negative for large $r$: attraction.
     - The potential goes to zero for large $r$: short-range.
     - The potential has a minimum of $-\varepsilon$ at $2^{1/6}\sigma$.
   - Computing all forces in an N-body system requires the computation of $N(N-1)/2$ (the number of pairs in the system) forces $\mathbf{F}_{ij}$
   - Computing forces is often the most demanding part of MD simulations.
   - A particle $i$ near the edge of the simulation box will feel a force from the periodic images, which can be closer to $i$ than their original counter-parts.
   - A consistent way to write the potential is

     $$U = \sum_{i,j,k} \sum_{n=1}^{N} \sum_{m=1}^{n-1} \varphi(|\mathbf{r}_n - \mathbf{r}_m + iL\hat{\mathbf{x}} + jL\hat{\mathbf{y}} + kL\hat{\mathbf{z}}|). \tag{4.9}$$

   - While this converges for most potentials $\varphi$, it is very impractical to have to compute an infinite sum to get the potential and forces.
   - To fix this, one can modify the potential such that it becomes zero beyond a certain *cut-off* distance $r_c$:

     $$\varphi'(r) = \begin{cases} \varphi(r) - \varphi(r_c) & \text{if } r < r_c \\ 0 & \text{if } r \geq r_c \end{cases}$$

     where the subtraction of $\varphi(r_c)$ is there to avoid discontinuities in the potential which would cause violations of energy conservation.

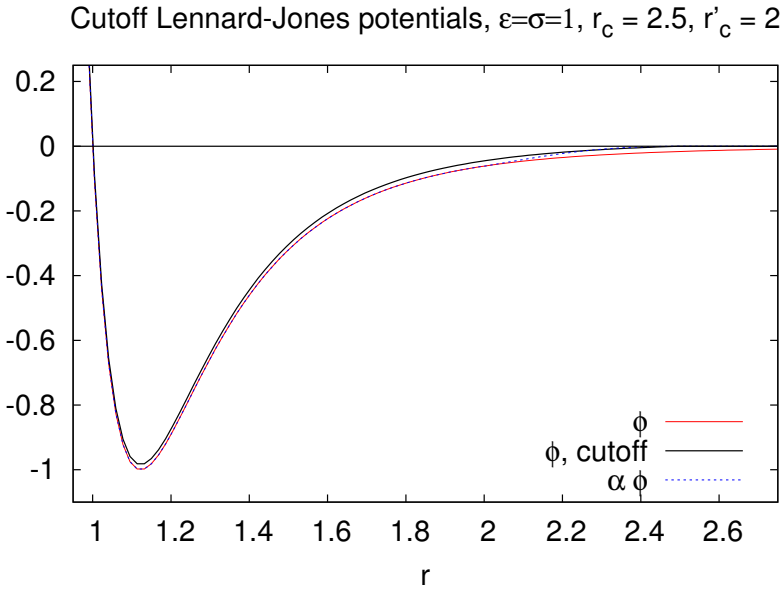
- To also avoid discontinuities in derivatives, one can use a schemes such as

$$\varphi''(r) = \alpha(r)\varphi(r) \tag{4.10}$$

where

$$\alpha(r) = \begin{cases} 1 & r < r_c' \\ \frac{(r_c - r)^2(r_c - 3r_c' + 2r)}{(r_c - r_c')^3} & r_c' \le r \le r_c \\ 0 & r > r_c \end{cases} . \tag{4.11}$$

Here is an example of these procedures applied to the Lennard-Jones potential:




- Once the potential is zero beyond a point, the sums over $i$, $j$, and $k$ in equation (4.9) become finite.
- In fact, if $r_c < L/2$, the sum contains at most one non-zero contribution for each pair of particles $(i, j)$. This pair is either in the same box, or one of them is in the adjacent boxes.
- For any pair, the correct distance vector can be found from the original distance vector $\mathbf{r} = \mathbf{r}_i - \mathbf{r}_j$ using equation (4.8).

3. *Initial conditions*

- The initial conditions are to some extend not important if the system naturally tends to equilibrium (ergodicity).
- Nonetheless, one would not want too extreme an initial configuration.

- Starting the system with the particles on a lattice and drawing initial momenta from a uniform or Gaussian distribution is typically a valid starting point.
- One often makes sure that the kinetic energy has the target value $\frac{3}{2}NkT$, while the total momentum is set to zero to avoid the system moving as a whole.

4. *Integration scheme*

   - Needed to solve the *dynamics* as given by the equations of motion.
   - Below, we will discuss in detail on how to construct or choose an appropriate integration scheme.

5. *Equilibration/Burn-in*

   - Since we do not start the system from an equilibrium state, a certain number of time steps are to be taken until the system has reached an equilibrium.
   - One can check for equilibrium by seeing if quantities like the potential energy are no longer changing in any systematic fashion and are just fluctuating around a mean values.
   - The equilibrium state is microcanonical at a given total energy $E_{tot} = E_{pot} + E_{kin}$.
   - Since $E_{kin} > 0$, the lattice initialization procedure outlined cannot reach all possible values of the energy, i.e. $E_{tot} > E_{pot}(lattice)$.
   - To reach lower energies, one can periodically rescale the momenta (a rudimentary form of a so called *thermostat*).
   - Another way to reach equilibrium is to generate initial conditions using the Monte Carlo method.

6. *Measurements*

   - Construct estimators for physical quantities of interest.
   - Since there are correlations along the simulated trajectory, one needs to take sample points that are far apart in time.
   - Although when one is interested in dynamical quantities, all points should be used. In the statistical analysis there correlations should be taken into account.

Given these ingredients, the outline of an MD simulation could look like this:

```
OUTLINE MD PROGRAM
SETUP INITIAL CONDITIONS
PERFORM EQUILIBRATION by INTEGRATING over a burn-in time B
SET time t to 0
PERFORM first MEASUREMENT
WHILE t < tfinal
    INTEGRATE over the measurement interval
    PERFORM MEASUREMENT
END WHILE
```

in which the integration step from t1 to t1+T looks as follows (assuming t=t1 at the start):

```
OUTLINE INTEGRATION
WHILE t < t1+T
     COMPUTE FORCES on all particles
     COMPUTE new positions and momenta according to INTEGRATION SCHEME
     APPLY PERIODIC BOUNDARY CONDITIONS
     UPDATE t to t+dt
END WHILE
```

Note: we will encounter integration schemes in which the forces need to be computed in intermediate steps, in which case the separation between force computation and integration is not as strict as this outline suggests.

### 4.1.3 Desirable qualities for a molecular dynamics integrator

- *Accuracy:*
  Accuracy means that the trajectory obeys the equations of motion to good approximation. This is a general demand that one would also impose on integrators for general differential equations. The accuracy in principle improves by decreasing the time step $\Delta t$. But because of the exponential separation of near-by trajectories in phase space (Lyapunov instability), this is of limited help.

  Furthermore, one cannot decrease $\Delta t$ too far in many particle systems for reasons of

- *Efficiency:*
  It is typically quite expensive to compute the inter-particle forces $F^N$, and taking smaller time steps $\Delta t$ requires more force evaluations per unit of physical time.

- *Respect physical laws:*
  - Time reversal symmetry
  - Conservation of energy
  - Conservation of linear momentum
  - Conservation of angular momentum
  - Conservation of phase space volume

  provided the simulated system also has these properties, of course.

  Violating these laws poses serious doubts on the ensemble that is sampled and on whether the trajectories are realistic.

  Unfortunately, there is no general algorithm that obeys all of these conservation laws exactly for an interacting many-particle system. At best, one can find time-reversible, volume preserving algorithms that conserve linear momentum and angular momentum, but that conserve the energy only approximately.

  Note furthermore that with periodic boundary conditions:
  - Translational invariance and thus conservation of momentum is preserved.
  - There is no wall potential, so the energy conservation is not affected either.
  - But rotational invariance is broken: No conservation of angular momentum.

- *Stability:*
  Given that the energy is only conserved approximately, when studying dynamics on large time scales, or when sampling phase space using MD, it is important that the simulation is stable, i.e., that the algorithm does not exhibit *energy drift*, since otherwise, it would not even sample the correct microcanonical energy shell.

Remarks:

- Since the computational cost thus limits the time step, the accuracy of the algorithm has to be assessed at a fixed time step.
- Since $\Delta t$ is not necessarily small, higher order algorithms need not be more accurate.
- The most efficient algorithm is then the one that allows the largest possible time step for a given level of accuracy, *while maintaining stability and preserving conservation laws.*

- All integration schemes become *numerically* unstable for large time steps $\Delta t$, even if they are stable at smaller time steps. A large step may can the system to a region of large potential energy. With infinite precision, this would just cause a large restoring force that pushes the system back into the low energy region. But with finite precision, the low energies cannot be resolved anymore, and the system remains in the high energy state.

- The dominance of the force evaluations means that the efficiency of a simulation can greatly be improved by streamlining the evaluation of the forces, using

  1. Cell divisions:

     - Divide the simulation box into cells larger than the cutoff $r_c$.
     - Make a list of all particles in each cell.
     - In the sum over pairs in the force computation, only sum pairs of particles in the same cell or in adjacent cells.
     - When 'adjacent' is properly defined, this procedure automatically picks out the right periodic image.
     - Draw-backs:
       1. needs at least three cells in any direction to be of use.
       2. Still summing many pairs that do not interact (corners).

  2. Neighbour lists (also called Verlet lists or Verlet neighbour lists):

     - Make a list of pairs of particles that are closer than $r_c + \delta r$: these are 'neighbours'.
     - Sum over the list of pairs to compute the forces.
     - The neighbour list are to be used in subsequent force calculations as long as the list is still valid.
     - Invalidation criterion: a particle has moved more than $\delta r/2$.
     - Therefore, before a new force computation, check if any particle has moved more than $\delta r/2$ since the last list-building. If so, rebuild the Verlet list, otherwise use the old one.
     - Notes:
       1. $\delta r$ needs to be chosen to balance the cost of rebuilding the list and considering non-interacting particles.
       2. The building of the list may be sped up by using cell divisions.

  For large systems, these methods of computing the interaction forces scale as $N$ instead of as $N^2$, as the naive implementation of summing over all pairs would give.

**Assessing the Euler scheme for the harmonic oscillator**

- Consider the Euler scheme applied to $x = (r, p)$, and $f(x, t) = (p, -r)$. i.e., (cf. equation (4.1))

$$\dot{r} = p$$
$$\dot{p} = -r.$$

This is the simple one-dimensional harmonic oscillator with mass 1 and frequency 1, whose solutions are oscillatory

$$r(t) = r(0)\cos t + p(0)\sin t \tag{4.12}$$
$$p(t) = p(0)\cos t - r(0)\sin t. \tag{4.13}$$

The Euler scheme (4.3) gives for this system

$$\begin{pmatrix} r_{n+1} \\ p_{n+1} \end{pmatrix} = \begin{pmatrix} 1 & \Delta t \\ -\Delta t & 1 \end{pmatrix} \begin{pmatrix} r_n \\ p_n \end{pmatrix}. \tag{4.14}$$

- The eigenvalues of the matrix on the right hand side of equation (4.14) are given by $\lambda_\pm = 1 \pm \mathrm{i}\Delta t$, and the solution of equation (4.14) can be expressed as

$$\begin{pmatrix} r_n \\ p_n \end{pmatrix} = \begin{pmatrix} 1 & \Delta t \\ -\Delta t & 1 \end{pmatrix}^n \begin{pmatrix} r_0 \\ \dot{p}_0 \end{pmatrix} \tag{4.15}$$
$$= \begin{pmatrix} \frac{1}{2}(\lambda_+^n + \lambda_-^n) & \frac{1}{2\mathrm{i}}(\lambda_+^n - \lambda_-^n) \\ \frac{-1}{2\mathrm{i}}(\lambda_+^n - \lambda_-^n) & \frac{1}{2}(\lambda_+^n + \lambda_-^n) \end{pmatrix} \begin{pmatrix} r_0 \\ p_0 \end{pmatrix} \tag{4.16}$$
$$= (\lambda_+\lambda_-)^{n/2} \begin{pmatrix} \frac{e^{i\omega' \Delta t n} + e^{-i\omega' \Delta t n}}{2} & \frac{e^{i\omega' \Delta t n} - e^{-i\omega' \Delta t n}}{2\mathrm{i}} \\ -\frac{e^{i\omega' \Delta t n} - e^{-i\omega' \Delta t n}}{2\mathrm{i}} & \frac{e^{i\omega' \Delta t n} + e^{-i\omega' \Delta t n}}{2} \end{pmatrix} \begin{pmatrix} r_0 \\ p_0 \end{pmatrix} \tag{4.17}$$
$$= (1 + \Delta t^2)^{\frac{t}{2\Delta t}} \begin{pmatrix} \cos(\omega' t) & \sin(\omega' t) \\ -\sin(\omega' t) & \cos(\omega' t) \end{pmatrix} \begin{pmatrix} r_0 \\ p_0 \end{pmatrix}, \tag{4.18}$$

where $e^{\mathrm{i}\omega' \Delta t} = (\lambda_+/\lambda_-)^{1/2}$. By comparing equations (4.13) and (4.18), we see that the behaviour of the numerical solution is similar to that of the real solution but with a different frequency, and with a prefactor which is larger than one and grows with time.

- Rather than performing a periodic, circular motion in phase space, the Euler scheme produces an outward spiral.

- *Accuracy*: $\omega' = \omega + \mathcal{O}(\Delta t)$ so this is only a first order integration scheme.

- *Time reversal invariant?* No.

- *Conserves energy?* No.
- *Conserves angular momentum?* No.
- *Conserves phase space?* No.
- *Stable?* No.

### 4.1.4 Verlet scheme

- If the system is governed by Newton's equations:

$$\dot{R}^N = \frac{1}{m} P^N$$
$$\dot{P}^N = F^N,$$

  then one can exploit the form of these equations to construct (better) integrators.

- The Verlet scheme is one of these schemes. It can be derived by Taylor expansion

$$R^N_{n-1} = R^N(t-\Delta t) = R^N_n - P^N_n \frac{\Delta t}{m} + F^N_n \frac{\Delta t^2}{2m} - \dddot{R}^N(t)\frac{\Delta t^3}{6} + \mathcal{O}(\Delta t^4)$$
$$R^N_{n+1} = R^N(t+\Delta t) = R^N_n + P^N_n \frac{\Delta t}{m} + F^N_n \frac{\Delta t^2}{2m} + \dddot{R}^N(t)\frac{\Delta t^3}{6} + \mathcal{O}(\Delta t^4).$$

  Adding these two equations leads to

$$R^N_{n-1} + R^N_{n+1} = 2R^N_n + F^N_n \frac{\Delta t^2}{m} + \mathcal{O}(\Delta t^4) \Rightarrow$$
$$\boxed{R^N_{n+1} = 2R^N_n - R^N_{n-1} + F^N_n \frac{\Delta t^2}{m}} \quad \underline{\textit{Position-only Verlet Integrator}} \tag{4.19}$$

- No momenta!
- Requires positions at the previous step!
- Simple algorithm (`r(i)` and `rprev(i)` are particle i's current and previous position)

```
VERLET ALGORITHM
SET time t to 0
WHILE t < tfinal
   COMPUTE the forces F(i) on all particles
   FOR each particle i
      COMPUTE new position rnew = 2*r(i)-rprev(i)+F(i)*dt*dt/m
```

```
        UPDATE previous position rprev(i) to r(i)
        UPDATE position r(i) to rnew
      END FOR
      UPDATE t to t+dt
    END WHILE
```

- Accuracy: This scheme is third order in the positions, so reasonably accurate.
- Respect physical laws?
  - Time reversal symmetry? Yes, since

$$R^N_{n-1} = 2R^N_n - R^N_{n+1} + F^N_n \frac{\Delta t^2}{m}.$$

  - Total energy conservation? No momenta, so energy conservation cannot be checked.
  - Linear momentum? Also not defined.
  - Angular momentum? Not defined.
  - Volume preserving? No phase space volume can be defined without momenta.
- Stability: very stable, no energy drift up to relatively large time steps. Why this is so will become clear later.

### 4.1.5 Leap Frog scheme

- Is a way to introduce momenta into the Verlet scheme.
- Define momenta at a 'half time step'

$$P^N_{n+1/2} = P^N(t + \Delta t/2) = m\frac{R^N_{n+1} - R^N_n}{\Delta t}. \tag{4.20}$$

- These momenta are correct up to $\mathcal{O}(\Delta t^2)$.
- If we get the positions from the Verlet scheme, then the errors in the momenta do not accumulate, so that the global order of the momenta in the Leap Frog method is also $\mathcal{O}(\Delta t^2)$.
- Given the half-step momenta, one may also perform the Leap Frog algorithm as follows:

$$R^N_{n+1} = R^N_n + P^N_{n+1/2}\frac{\Delta t}{m} \text{ (which follows from (4.20))},$$

where

$$P^N_{n+1/2} = m\frac{R^N_{n+1} - R^N_n}{\Delta t} = m\frac{R^N_n - R^N_{n-1} + R^N_{n+1} + R^N_{n-1} - 2R^N_n}{\Delta t}$$
$$= P^N_{n-1/2} + F^N_n \Delta t \text{ (as follows from (4.19)).}$$

- The scheme is thus:

$$\boxed{\begin{aligned} P^N_{n+1/2} &= P^N_{n-1/2} + F^N_n \Delta t \\ R^N_{n+1} &= R^N_n + P^N_{n+1/2}\frac{\Delta t}{m} \end{aligned}} \quad \underline{\textit{Leap Frog integrator.}} \tag{4.21}$$

- Since the Leap Frog algorithm is derived from the Verlet scheme, it is equally stable.
- The Leap Frog algorithm has the appearance of a first order Taylor expansion, but because of the half-step momenta, it is third order in positions and second order in momenta.
- Since momenta are defined at different time points than positions, conservation laws (energy, momentum,...) can still not be checked.
- The Leap Frog scheme is easy to implement:

```
LEAP-FROG ALGORITHM
SET time t to 0
WHILE t < tfinal
   COMPUTE the forces F(i) on all particles
   FOR each particle i
      UPDATE momentum p(i) to p(i)+F(i)*dt
      UPDATE position r(i) to r(i)+p(i)*dt/m
   END FOR
   UPDATE t to t+dt
END WHILE
```

### 4.1.6 Momentum/Velocity Verlet scheme

- This scheme will integrate positions and momenta (or velocities) at the same time points, while keeping the position equivalence with the original Verlet scheme.
- We define the momenta at time $t = n\Delta t$ as

$$P^N_n = \frac{1}{2}\left(P^N_{n+1/2} + P^N_{n-1/2}\right).$$

- Using that the half step momenta are correct to $O(\Delta t^2)$, we see that this is also correct to that order, since

$$\begin{aligned}
&\frac{1}{2}\left[P^N\left(t+\frac{\Delta t}{2}\right)+P^N\left(t-\frac{\Delta t}{2}\right)\right] \\
&=\frac{1}{2}\left[P^N(t)+F_n^N\frac{\Delta t}{2}+P^N(t)-F_n^N\frac{\Delta t}{2}+\mathcal{O}(\Delta t^2)\right] \\
&=P^N(t)+\mathcal{O}(\Delta t^2).
\end{aligned}$$

- Using the momentum rule of the Leap Frog algorithm

$$P^N_{n+1/2}=P^N_{n-1/2}+F^N_n\Delta t,$$

and the definition of $P^N_n$, one gets

$$P^N_{n+1/2}=2P^N_n-P^N_{n+1/2}+F^N_n\Delta t,$$

or

$$P^N_{n+1/2}=P^N_n+F^N_n\frac{\Delta t}{2}. \tag{4.22}$$

Substituting Eq. (4.22) into the position rule of the Leap Frog gives the position transformation in the momentum-Verlet scheme

$$R^N_{n+1}=R^N_n+P^N_n\frac{\Delta t}{m}+F^N_n\frac{\Delta t^2}{2m}.$$

- The corresponding momentum rule is found using the definition of the momentum and the momentum rule of the Leap Frog:

$$\begin{aligned}
P^N_{n+1}&=\frac{1}{2}[P^N_{n+3/2}+P^N_{n+1/2}] \\
&=\frac{1}{2}[P^N_{n+1/2}+F^N_{n+1}\Delta t+P^N_{n+1/2}] \\
&=P^N_{n+1/2}+F^N_{n+1}\frac{\Delta t}{2} \\
&=P^N_n+\frac{F^N_{n+1}+F^N_n}{2}\Delta t,
\end{aligned} \tag{4.23}$$

where (4.22) was used.

- This algorithm is usually called velocity Verlet, and is then expressed in terms of the velocities $V^N=P^N/m$.

- Summarizing:

$$\boxed{\begin{aligned} R^N_{n+1} &= R^N_n + \frac{P^N_n}{m}\Delta t + \frac{F^N_n}{2m}\Delta t^2 \\ P^N_{n+1} &= P^N_n + \frac{F^N_{n+1} + F^N_n}{2}\Delta t \end{aligned}} \quad \underline{\textit{Momentum Verlet Scheme (first version).}}$$

- The momentum rule appears to pose a problem since $F^N_{n+1}$ is required. But to compute $F^N_{n+1}$, we need only $R^N_{n+1}$, which is computed in the integration step as well. That is, given that the forces are known at step $n$, the next step is can be taken by

```
STORE all the forces F(i) as Fprev(i)
FOR each particle i
   UPDATE position r(i) to r(i)+p(i)*dt/m+F(i)*dt*dt/(2*m)
END FOR
RECOMPUTE the forces F(i) using the updated positions
FOR each particle i
   UPDATE momentum p(i) to p(i)+(F(i)+Fprev(i))*dt/2
END FOR
```

- The extra storage step can be avoided by reintroducing the half step momenta as intermediates. From Eqs. (4.21) (first line), (4.23) and (4.22), one finds

$$\boxed{\begin{aligned} P^N_{n+1/2} &= P^N_n + \frac{1}{2}F^N_n\Delta t \\ R^N_{n+1} &= R^N_n + \frac{P^N_{n+1/2}}{m}\Delta t \\ P^N_{n+1} &= P^N_{n+1/2} + \frac{1}{2}F^N_{n+1}\Delta t \end{aligned}} \quad \underline{\textit{Momentum Verlet Scheme, second version.}}$$

(4.24)

- In pseudo-code:

```
MOMENTUM-VERLET ALGORITHM
SET time t to 0
COMPUTE the forces F(i)
WHILE t < tfinal
   FOR each particle i
      UPDATE momentum p(i) to p(i)+F(i)*dt/2
      UPDATE position r(i) to r(i)+p(i)*dt/m
   END FOR
   UPDATE t to t+dt
   RECOMPUTE the forces F(i)
   FOR each particle i
      UPDATE momentum p(i) to p(i)+F(i)*dt/2
   END FOR
END WHILE
```

## 4.2 Symplectic integrators from Hamiltonian splitting methods

- For sampling, one wants a long trajectory (formally $t_f \to \infty$).

- It is therefore important that an integration algorithm be stable.

- The instability of the Euler scheme is general, so generally, one would not use it.

- The momentum Verlet scheme, on the other hand, is much more stable.

- To see why, we will re-derive the momentum Verlet scheme from a completely different starting point, using a so-called *Hamiltonian splitting method* (also known as *Geometric integration*).

- We return to the formulation of the equations of motion using the Liouville operator:

$$\dot{X}^N = \mathcal{L}X^N, \tag{4.25}$$

where the Liouville operator $\mathcal{L}$ acting on a phase space function $A$ was defined in terms

of the Poison bracket as

$$\begin{aligned}\mathcal{L}A &= \{A, \mathcal{H}\} \\ &= \frac{\partial A}{\partial R^N} \cdot \frac{\partial H}{\partial P^N} - \frac{\partial H}{\partial R^N} \cdot \frac{\partial A}{\partial P^N} \\ &= \left( \frac{\partial \mathcal{H}}{\partial P^N} \cdot \frac{\partial}{\partial R^N} - \frac{\partial \mathcal{H}}{\partial R^N} \cdot \frac{\partial}{\partial P^N} \right) A = \left( \left[ \mathsf{J} \cdot \frac{\partial \mathcal{H}}{\partial X^N} \right]^T \cdot \frac{\partial}{\partial X^N} \right) A,\end{aligned}$$

where $\mathsf{J}$ is the symplectic matrix

$$\mathsf{J} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}.$$

- Remembering that the Hamiltonian $\mathcal{H}$ was defined as

$$\mathcal{H} = \frac{P^N \cdot P^N}{2m} + U(R^N), \tag{4.26}$$

it is easy to show that (4.25) leads to

$$\boxed{\dot{X}^N = \mathsf{J} \cdot \frac{\partial H}{\partial X^N}} \tag{4.27}$$

which are just Newton's equation of motion

$$\dot{R}^N = P^N/m; \qquad \dot{P}^N = -F^N = -\frac{\partial U}{\partial R^N}.$$

- Equations of motion of the form equation (4.27) are called symplectic.
- Symplecticity of the equations of motion has a number of important implications:

1. Symplecticity implies Liouville's theorem, i.e., conservation of phase space volume, because the rate by which phase space volume changes is given by the divergence of the flow in phase space, and

$$\frac{\partial}{\partial X^N} \cdot \dot{X}^N = \frac{\partial}{\partial X^N} \cdot \left[ \mathsf{J} \cdot \frac{\partial \mathcal{H}}{\partial X^N} \right] = \mathsf{J} : \frac{\partial^2 \mathcal{H}}{\partial X^N X^N} = 0$$

since $J$ is an antisymmetric matrix and $\frac{\partial^2 \mathcal{H}}{\partial X^N X^N}$ is symmetric.

2. If the Hamiltonian is independent of time, symplecticity implies conservation of energy $\mathcal{H}$, since

$$\frac{d\mathcal{H}}{dt} = \left[ \frac{\partial \mathcal{H}}{\partial X^N} \right]^T \cdot \dot{X}^N = \left[ \frac{\partial \mathcal{H}}{\partial X^N} \right]^T \cdot \mathsf{J} \cdot \frac{\partial \mathcal{H}}{\partial X^N} = 0,$$

again using the antisymmetry of $\mathsf{J}$.

3. If the Hamiltonian is invariant under time reversal (i.e., even in momenta), then symplecticity implies time-reversibility.
Time reversal means reversing the momenta, which will be denoted by an operator $\mathcal{T}$. Time reversal symmetry means that

$$\mathcal{T} e^{\mathcal{L}t} \mathcal{T} = \left[e^{\mathcal{L}t}\right]^{-1} = e^{-\mathcal{L}t}.$$

The infinitesimal-$t$ version of this is

$$\mathcal{T}\mathcal{L}\mathcal{T} = -\mathcal{L}$$

When acting on a phase space point $X^N = (R^N, P^N)$, one may also write

$$\mathcal{T} X^N = \mathsf{T} \cdot X^N,$$

where the symmetric matrix

$$\mathsf{T} = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -1 \end{pmatrix}.$$

was defined. Similarly, for derivative one has

$$\mathcal{T} \frac{\partial}{\partial X^N} = \mathsf{T} \cdot \frac{\partial}{\partial X^N},$$

i.e.

$$\mathcal{T} \frac{\partial}{\partial X^N} A = \mathsf{T} \cdot \frac{\partial}{\partial X^N} \mathcal{T} A,$$

One easily shows that the $\mathsf{T}$ matrix and the symplectic matrix anti-commute

$$\mathsf{T} \cdot \mathsf{J} = -\mathsf{J} \cdot \mathsf{T}.$$

This property, when combined with a $\mathcal{T}$-invariant Hamiltonian, implies time-

reversal, since

$$\begin{aligned}
\mathcal{T}\mathcal{L}\mathcal{T} &= \mathcal{T}\left(\mathsf{J}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\frac{\partial}{\partial X^N}\mathcal{T}\\
&= \mathcal{T}\left(\mathsf{J}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\mathcal{T}\mathsf{T}\cdot\frac{\partial}{\partial X^N}\\
&= \mathcal{T}\mathcal{T}\left(\mathsf{J}\cdot\mathsf{T}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\mathsf{T}\cdot\frac{\partial}{\partial X^N}\\
&= \left(\mathsf{J}\cdot\mathsf{T}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\mathsf{T}\cdot\frac{\partial}{\partial X^N}\\
&= -\left(\mathsf{T}\cdot\mathsf{J}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\mathsf{T}\cdot\frac{\partial}{\partial X^N}\\
&= -\left(\mathsf{J}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\mathsf{T}^T\cdot\mathsf{T}\cdot\frac{\partial}{\partial X^N}\\
&= -\left(\mathsf{J}\cdot\frac{\partial\mathcal{H}}{\partial X^N}\right)^T\cdot\frac{\partial}{\partial X^N}\\
&= -\mathcal{L} \qquad \text{q.e.d.}
\end{aligned}$$

- The idea is now to construct symplectic integrators, such that (by construction), they conserve phase space volume, conserve momentum and linear momentum when applicable and are time-reversible.

- Remember that the formal solution of the equations of motions in equation (4.25) is

  $$X^N(t) = e^{\mathcal{L}t}X^N(0),$$

  but this exponent can only be evaluated explicitly for exceptional forms of $\mathcal{L}$, such as for

  - free particles (e.g. an ideal gas),
  - systems with harmonic forces (e.g. particles harmonically bound on a lattice), and
  - free rigid bodies.

- Thus, for a Hamiltonian without the potential in (4.26), which is just the kinetic energy

  $$K = \frac{P^N\cdot P^N}{2m},$$

one has

$$\mathcal{L}_K = \left( \mathsf{J} \cdot \frac{\partial K}{\partial X^N} \right)^T \cdot \frac{\partial}{\partial X^N} \quad = \frac{P^N}{m} \cdot \frac{\partial}{\partial R^N},$$

the exponentiated Liouville operator $e^{\mathcal{L}_K t}$ corresponds to free motion:

$$e^{\mathcal{L}_K t} A(R^N, P^N) = A\left( R^N + \frac{P^N}{m} t,\, P^N \right).$$

We call this a free propagation over a time $t$.

- For a Liouville operator composed of just the potential energy,

$$\mathcal{L}_U = \left( \mathsf{J} \cdot \frac{\partial U}{\partial X^N} \right)^T \cdot \frac{\partial}{\partial X^N} \;\; = F^N \cdot \frac{\partial}{\partial P^N}$$

one can also evaluate the exponential

$$e^{\mathcal{L}_U t} A(R^N, P^N) = A\left( R^N, P^N + F^N t \right).$$

We will call this a force propagation over a time $t$.

- Although we can solve the exponent of the operators $\mathcal{L}_K$ and $\mathcal{L}_U$ separately, we cannot exponentiate their sum, because

$$e^{X+Y} \neq e^X e^Y$$

when $X$ and $Y$ are non-commuting operators. The operators $\mathcal{L}_K$ and $\mathcal{L}_U$ do not commute since

$$\begin{aligned}
[\mathcal{L}_K, \mathcal{L}_U] &= \mathcal{L}_K \mathcal{L}_U - \mathcal{L}_U \mathcal{L}_K \\
&= P^N \cdot \frac{\partial}{\partial R^N} F^N \cdot \frac{\partial}{\partial P^N} - F^N \cdot \frac{\partial}{\partial P^N} P^N \cdot \frac{\partial}{\partial R^N} \\
&= P^N \cdot \left( \frac{\partial F^N}{\partial R^N} \right) \cdot \frac{\partial}{\partial P^N} - F^N \cdot \frac{\partial}{\partial R^N} \\
&\neq 0.
\end{aligned}$$

- We can however use the Baker-Campbell-Hausdorff (BCH) formula

$$e^X e^Y = e^{X+Y+\frac{1}{2}[X,Y]+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\text{further repeated commutators of } X \text{ and } Y}. \quad (4.28)$$

In the current context this is useful if $X$ and $Y$ are small, so that repeated commutators become successively smaller. This smallness can be achieved by taking $M = t/\Delta t$ small time steps, as follows:

$$e^{\mathcal{L}t} = e^{\mathcal{L}\Delta t (t/\Delta t)} = \left[ e^{\mathcal{L}\Delta t} \right]^{t/\Delta t} = \left[ e^{\mathcal{L}_K \Delta t + \mathcal{L}_U \Delta t} \right]^M. \quad (4.29)$$

- Now let $X = \mathcal{L}_U \Delta t$ and $Y = \mathcal{L}_K \Delta t$, then $[X, Y] = \mathcal{O}(\Delta t^2)$, $[X, [X, Y]] = \mathcal{O}(\Delta t^3)$ etc.
- Denote any repeated commutators by $\ldots$, then the BCH formula gives

$$\begin{aligned} e^X e^Y e^{-\frac{1}{2}[X,Y]} &= e^{X+Y+\frac{1}{2}[X,Y]+\ldots} e^{-\frac{1}{2}[X,Y]} \\ &= e^{X+Y+\frac{1}{2}[X,Y]-\frac{1}{2}[X,Y]+\frac{1}{2}[X+Y+\frac{1}{2}[X,Y],-\frac{1}{2}[X,Y]]+\ldots} \\ &= e^{X+Y+\frac{1}{2}[X+Y+\frac{1}{2}[X,Y],-\frac{1}{2}[X,Y]]+\ldots} \\ &= e^{X+Y+\ldots} \end{aligned}$$

- Since $\ldots = \mathcal{O}(\Delta t^3)$ and $[X, Y] = \mathcal{O}(\Delta t^2)$, we see that

$$e^{\mathcal{L}\Delta t} = e^{\mathcal{L}_U \Delta t} e^{\mathcal{L}_K \Delta t} + \mathcal{O}(\Delta t^2) \tag{4.30}$$

- Using this in Eq. (4.29) would give a scheme in which alternating force and free propagation is performed over small time steps $\Delta t$.
- The accumulated error of this scheme is $\mathcal{O}(\Delta t)$, but the Verlet scheme was $\mathcal{O}(\Delta t^2)$.
- The missing ingredient is time reversal. Note that while the true propagation satisfies time reversal invariance:

$$\mathcal{T} e^{\mathcal{L}_U \Delta t + \mathcal{L}_K \Delta t} \mathcal{T} = \left[ e^{\mathcal{L}_U \Delta t + \mathcal{L}_K \Delta t} \right]^{-1}.$$

  Due to the symplecticity of the $\mathcal{L}_U \Delta t$ and $\mathcal{L}_K \Delta t$ operators separately, the approximate evolution has

$$\mathcal{T} e^{\mathcal{L}_U \Delta t} e^{\mathcal{L}_K \Delta t} \mathcal{T} = \mathcal{T} e^{\mathcal{L}_U \Delta t} \mathcal{T} \mathcal{T} e^{\mathcal{L}_K \Delta t} \mathcal{T} = e^{-\mathcal{L}_U \Delta t} e^{-\mathcal{L}_K \Delta t},$$

  which is *not* equal to the inverse

$$\left[ e^{\mathcal{L}_U \Delta t} e^{\mathcal{L}_K \Delta t} \right]^{-1} = e^{-\mathcal{L}_K \Delta t} e^{-\mathcal{L}_U \Delta t}.$$

- Time reversal can be restored by taking

$$e^{\mathcal{L}_U \Delta t + \mathcal{L}_K \Delta t} = e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t} e^{\mathcal{L}_U \Delta t/2} + \ldots, \tag{4.31}$$

  since

$$\begin{aligned} \mathcal{T} e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t} e^{\mathcal{L}_U \Delta t/2} \mathcal{T} &= \mathcal{T} e^{\mathcal{L}_U \Delta t/2} \mathcal{T} \mathcal{T} e^{\mathcal{L}_K \Delta t} \mathcal{T} \mathcal{T} e^{\mathcal{L}_U \Delta t/2} \mathcal{T} \\ &= e^{-\mathcal{L}_U \Delta t/2} e^{-\mathcal{L}_K \Delta t} e^{-\mathcal{L}_U \Delta t/2} \\ &= \left[ e^{-\mathcal{L}_U \Delta t/2} e^{-\mathcal{L}_K \Delta t} e^{-\mathcal{L}_U \Delta t/2} \right]^{-1} \end{aligned}$$

- Equation (4.31) is actually of higher order than equation (4.30), as one sees from applying the BCH formula

$$\begin{aligned} e^{\mathcal{L}_U\Delta t+\mathcal{L}_K\Delta t} &= e^{\mathcal{L}_U\Delta t/2+\mathcal{L}_K\Delta t+\mathcal{L}_U\Delta t/2} \\ &= e^{\mathcal{L}_U\Delta t/2+\mathcal{L}_K\Delta t}e^{-\frac{1}{2}[\mathcal{L}_U\Delta t/2+\mathcal{L}_K\Delta t,\mathcal{L}_U\Delta t/2]+\dots}e^{\mathcal{L}_U\Delta t/2} \\ &= e^{\mathcal{L}_U\Delta t/2+\mathcal{L}_K\Delta t}e^{-\frac{1}{4}[\mathcal{L}_K\Delta t,\mathcal{L}_U\Delta t]+\dots}e^{\mathcal{L}_U\Delta t/2} \\ &= e^{\mathcal{L}_U\Delta t/2}e^{\mathcal{L}_K\Delta t}e^{-\frac{1}{2}[\mathcal{L}_U\Delta t/2,\mathcal{L}_K\Delta t]+\dots}e^{-\frac{1}{4}[\mathcal{L}_K\Delta t,\mathcal{L}_U\Delta t]+\dots}e^{\mathcal{L}_U\Delta t/2} \\ &= e^{\mathcal{L}_U\Delta t/2}e^{\mathcal{L}_K\Delta t}e^{-\frac{1}{4}[\mathcal{L}_U\Delta t,\mathcal{L}_K\Delta t]+\dots}e^{-\frac{1}{4}[\mathcal{L}_K\Delta t,\mathcal{L}_U\Delta t]+\dots}e^{\mathcal{L}_U\Delta t/2} \\ &= e^{\mathcal{L}_U\Delta t/2}e^{\mathcal{L}_K\Delta t}e^{\cdots}e^{\mathcal{L}_U\Delta t/2} \end{aligned}$$

  Remember that $\dots$ was $\mathcal{O}(\Delta t^3)$, so this scheme has a third order local error and consequently a second order global error.

- The scheme in equation (4.31) is our momentum Verlet scheme that we had derived before, see equation (4.24). It first performs a half force propagation, a whole free propagation and then another half force propagation.

- The splitting method is more general than what we have just derived. One does not *have* to split up the Hamiltonian into the kinetic and potential part. All that is required is that the separate sub-Hamiltonian can be explicitly exponentiated.

- The following general construction of a splitting scheme is as follows

  1. Split the Hamiltonian $H$ up into $n$ partial Hamiltonians $\mathcal{H}_1$, $\mathcal{H}_2$, $\dots$ $\mathcal{H}_n$:

$$\mathcal{H} = \sum_{j=1}^{n} \mathcal{H}_j.$$

     In more advanced splitting schemes, one may in addition define auxiliary Hamiltonians $\mathcal{H}_{j>n}$ which do not enter in $\mathcal{H}$.

  2. Associate with each partial Hamiltonian $\mathcal{H}_j$ a partial Liouville operator

$$\mathcal{L}_j = \mathcal{L}_{\mathcal{H}_j} = \left[\mathsf{J}\cdot\frac{\partial\mathcal{H}_j}{\partial X^N}\right]^T\cdot\frac{\partial}{\partial X^N}$$

     such that the full Liouvillean is given by

$$\mathcal{L} = \sum_{j=1}^{n} \mathcal{L}_j.$$

3. One splits up the exponentiated Liouvillean in $S$ factors

$$e^{\mathcal{L}\Delta t} = e^{\sum_{j=1}^{n} \mathcal{L}_j \Delta t} \approx \prod_{s=1}^{S} e^{\mathcal{L}_{j_s} \Delta t_s}, \tag{4.32}$$

where the product is taken left-to-right, such that the first factor on the left is $s = 1$ while the last on the right is $s = S$.

4. Since each Liouvillean is multiplied by a total time interval $\Delta t$ in the original exponent, the separate time intervals for each Liouvillean $\mathcal{L}_{j'}$ have to add up to $\Delta t$ as well, at least up to the order of the scheme

$$\sum_{\substack{s=1 \\ \text{with } j_s = j'}}^{S} \Delta t_s = \Delta t + \mathcal{O}(\Delta t^{k+1}).$$

for each $j' = 1 \ldots n$.
For auxiliary Hamiltonians $\mathcal{H}_{j>n}$, their combined time steps should be zero up to the order of the scheme:

$$\sum_{\substack{s=1 \\ \text{with } j_s = j'}}^{S} \Delta t_s = 0 + \mathcal{O}(\Delta t^{k+1}).$$

for $j' > n$.

5. One should take $t_{S+1-s} = t_s$ and $j_{S+1-s} = t_s$ in order to have time reversal invariance (we will assume that the $\mathcal{H}_j$ are invariant under time reversal).

6. One uses the BCH formula to adjust the $\Delta t_s$ further, such that

$$e^{\mathcal{L}\Delta t} = \prod_{s=1}^{P} e^{\mathcal{L}_{j_s} \Delta t_s} + \mathcal{O}(\Delta t^{k+1}) \tag{4.33}$$

which would make this scheme of order $k$.

- Properties:
  - Symplectic ⇒ phase space volume preserving.
  - Given 4., also time reversible. Proof:

$$\mathcal{T}\left[\prod_{s=1}^{S} e^{\mathcal{L}_{j_s}\Delta t_s}\right]\mathcal{T} = \prod_{s=1}^{S}\left[\mathcal{T} e^{\mathcal{L}_{j_s}\Delta t_s}\mathcal{T}\right] = \prod_{s=1}^{S} e^{-\mathcal{L}_{j_s}\Delta t_s}$$
$$= \prod_{s=1}^{S}\left[e^{\mathcal{L}_{j_s}\Delta t_s}\right]^{-1} = \left[\prod_{s=S}^{1} e^{\mathcal{L}_{j_s}\Delta t_s}\right]^{-1} = \left[\prod_{s=1}^{S} e^{\mathcal{L}_{j_s}\Delta t_s}\right]^{-1}$$

– The scheme is of even order: Reason: the scheme is time reversible, so each error found by applying the BCH formula must also be time-reversible, i.e., each term $X$ in the exponent satisfies $\mathcal{T}X\mathcal{T} = -X$. Thus, the error terms are odd in the partial Liouvilleans. Since each Liouvillean comes with a factor of $\Delta t$, the local error terms are odd in $\Delta t$.
The resulting global error is then even in $\Delta t$.

– If the full Hamiltonian conserves a quantity $Q$, i.e. $\{\mathcal{H}, Q\} = 0$, and if also each partial Hamiltonian $\mathcal{H}_j$ also satisfies $\{\mathcal{H}_j, Q\} = 0$, then the quantity $Q$ is conserved in each step in equation (4.32), and thus exactly conserved in the integration scheme.

## 4.3 The shadow or pseudo-Hamiltonian

- Energy $\mathcal{H}$ is rarely conserved in integration schemes, even symplectic ones.
- Nonetheless, the energy is almost conserved. We will now see in what sense.
- In the derivation of the splitting schemes, we used that repeated commutators of small-time step Liouvilleans are higher order corrections, so that they may be omitted.
- In fact, one can show that the commutator of two Liouvilleans $\mathcal{L}_{\mathcal{H}_1}$ and $\mathcal{L}_{\mathcal{H}_2}$ associated with two Hamiltonians $\mathcal{H}_1$ and $\mathcal{H}_2$ is again a Liouvillean of another Hamiltonian:

$$\begin{aligned}[\mathcal{L}_{\mathcal{H}_1}, \mathcal{L}_{\mathcal{H}_2}]A &= \mathcal{L}_{\mathcal{H}_1}\mathcal{L}_{\mathcal{H}_2}A - \mathcal{L}_{\mathcal{H}_2}\mathcal{L}_{\mathcal{H}_1}A \\ &= \mathcal{L}_{\mathcal{H}_1}\{A, \mathcal{H}_2\} - \mathcal{L}_{\mathcal{H}_2}\{A, \mathcal{H}_1\} \\ &= \{\{A, \mathcal{H}_2\}, \mathcal{H}_1\} - \{\{A, \mathcal{H}_1\}, \mathcal{H}_2\} \\ &= \{\{A, \mathcal{H}_2\}, \mathcal{H}_1\} + \{\{\mathcal{H}_1, A\}, \mathcal{H}_2\}.\end{aligned}$$

Using the Jacobi identity for Poisson brackets

$$\{\{A, B\}, C\} + \{\{B, C\}, A\} + \{\{C, A\}, B\} = 0,$$

we find

$$[\mathcal{L}_{\mathcal{H}_1}, \mathcal{L}_{\mathcal{H}_2}]A = \{\{\mathcal{H}_2, \mathcal{H}_1\}, A\}$$

so that

$$[\mathcal{L}_{\mathcal{H}_1}, \mathcal{L}_{\mathcal{H}_2}] = \mathcal{L}_{\{\mathcal{H}_2, \mathcal{H}_1\}}.$$

- Consider now the Verlet splitting scheme, writing for brevity $X = \mathcal{L}_U \Delta t/2$ and $Y = \mathcal{L}_K \Delta t$ and using the BCH formula to one order further than before:

$$\begin{aligned}
e^X e^Y e^X &= e^{X+Y+\frac{1}{2}[X,Y]+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\ldots} e^X \\
&= e^{X+Y+\frac{1}{2}[X,Y]+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+X+\frac{1}{2}[X+Y+\frac{1}{2}[X,Y],X]+\frac{1}{12}[X+Y,[X+Y,X]]+\frac{1}{12}[X,[X,X+Y]]+\ldots} \\
&= e^{2X+Y+\frac{1}{2}[X,Y]+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\frac{1}{2}[Y+\frac{1}{2}[X,Y],X]+\frac{1}{12}[X+Y,[Y,X]]+\frac{1}{12}[X,[X,Y]]+\ldots} \\
&= e^{2X+Y+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\frac{1}{2}[\frac{1}{2}[X,Y],X]+\frac{1}{12}[X+Y,[Y,X]]+\frac{1}{12}[X,[X,Y]]+\ldots} \\
&= e^{2X+Y+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\frac{1}{4}[[X,Y],X]+\frac{1}{12}[X,[Y,X]]+\frac{1}{12}[Y,[Y,X]]+\frac{1}{12}[X,[X,Y]]+\ldots} \\
&= e^{2X+Y+\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]-\frac{1}{4}[X,[X,Y]]-\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\frac{1}{12}[X,[X,Y]]+\ldots} \\
&= e^{2X+Y+\frac{1}{12}[X,[X,Y]]-\frac{1}{4}[X,[X,Y]]+\frac{1}{12}[X,[X,Y]]-\frac{1}{12}[X,[X,Y]]+\frac{1}{12}[Y,[Y,X]]+\frac{1}{12}[Y,[Y,X]]+\ldots} \\
&= e^{2X+Y-\frac{1}{6}[X,[X,Y]]+\frac{1}{6}[Y,[Y,X]]+\ldots} \qquad (4.34)
\end{aligned}$$

Re-substituting $X$ and $Y$, we get

$$\begin{aligned}
e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t} e^{\mathcal{L}_U \Delta t/2} &= e^{\mathcal{L}_\mathcal{H} \Delta t - \frac{1}{24}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]]\Delta t^3 + \frac{1}{12}[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]\Delta t^3 + \mathcal{O}(\Delta t^5)} \\
&= e^{\left\{\mathcal{L}_\mathcal{H} - \frac{1}{24}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]]\Delta t^2 + \frac{1}{12}[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]\Delta t^2 + \mathcal{O}(\Delta t^4)\right\}\Delta t}
\end{aligned}$$

This is the evolution belonging to the following operator

$$\begin{aligned}
\mathcal{L}_{\text{shadow}} &= \mathcal{L}_\mathcal{H} - \frac{1}{24}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]]\Delta t^2 + \frac{1}{12}[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]\Delta t^2 + \mathcal{O}(\Delta t^4) \\
&= \mathcal{L}_\mathcal{H} - \frac{1}{24}[\mathcal{L}_U,\mathcal{L}_{\{K,U\}}]\Delta t^2 + \frac{1}{12}[\mathcal{L}_K,\mathcal{L}_{\{U,K\}}]\Delta t^2 + \mathcal{O}(\Delta t^4) \\
&= \mathcal{L}_\mathcal{H} - \frac{1}{24}\mathcal{L}_{\{\{K,U\},U\}}\Delta t^2 + \frac{1}{12}\mathcal{L}_{\{\{U,K\},K\}}\Delta t^2 + \mathcal{O}(\Delta t^4) \\
&= \mathcal{L}_{\mathcal{H}_{\text{pseudo}}},
\end{aligned}$$

where the pseudo-Hamiltonian or shadow Hamiltonian is

$$\mathcal{H}_{\text{pseudo}} = \mathcal{H} - \frac{1}{24}\{\{K,U\},U\}\Delta t^2 + \frac{1}{12}\{\{U,K\},K\}\Delta t^2 + \mathcal{O}(\Delta t^4).$$

If $\mathcal{H}$ is of the form $|P^N|^2/(2m) + U(R^N)$, one has

$$\{\{K,U\},U\} = \frac{\partial U}{\partial R^N} \cdot \frac{\partial^2 K}{\partial P^N \partial P^N} \cdot \frac{\partial U}{\partial R^N} = \frac{1}{m}\left|\frac{\partial U}{\partial R^N}\right|^2 = \frac{1}{m}|F^N|^2 \qquad (4.35)$$

$$\{\{U,K\},K\} = \frac{\partial K}{\partial P^N} \cdot \frac{\partial^2 U}{\partial R^N \partial R^N} \cdot \frac{\partial K}{\partial P^N} = \frac{1}{m^2} P^N \cdot \frac{\partial^2 U}{\partial R^N \partial R^N} \cdot P^N, \qquad (4.36)$$

so that

$$\mathcal{H}_{\text{pseudo}} = \mathcal{H} - \frac{1}{24m}\frac{\partial U}{\partial R^N} \cdot \frac{\partial U}{\partial R^N} + \frac{1}{12m^2} P^N \cdot \frac{\partial^2 U}{\partial R^N \partial R^N} \cdot P^N + \mathcal{O}(\Delta t^4). \qquad (4.37)$$

$\Rightarrow$ *The leading correction to the scheme is of Hamiltonian form.*

- This could be worked out to any order in $\Delta t$, and because commutators of Liouvilleans are Liouvilleans themselves, one would always find that the correction terms to the integration scheme can in principle be taken together into a pseudo-Hamiltonian:

  $$e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t/2} e^{\mathcal{L}_U \Delta t/2} = e^{\mathcal{L}_{\mathcal{H}_{\text{pseudo}}} \Delta t}$$

  where

  $$\mathcal{H}_{\text{pseudo}} = \sum_{h=0}^{\infty} \mathcal{H}_h \Delta t^h, \tag{4.38}$$

  with all odd $\mathcal{H}_h$ zero and

  $$\mathcal{H}_0 = K + U = \mathcal{H}$$
  $$\mathcal{H}_2 = -\frac{1}{24}\{\{K,U\},U\} + \frac{1}{12}\{\{U,K\},K\}.$$

- For a general splitting scheme (4.33), there is also a pseudo-Hamiltonian, although the expressions for the $\mathcal{H}_h$ differ (except for $\mathcal{H}_0$ which is always $\mathcal{H}$).
  If the scheme is of order $k$, all $\mathcal{H}_h$ with $0 < h < k$ vanish.

- We conclude that for schemes derived from Hamiltonian splitting schemes, the dynamics in the simulation is that corresponding to the pseudo-Hamiltonian rather than the real Hamiltonian.

- Since the dynamics generated by the splitting scheme is that of the pseudo-Hamiltonian, the value of the pseudo-Hamiltonian is conserved in the dynamics.

- Because the real Hamiltonian and the pseudo-Hamiltonian differ by an amount $\mathcal{O}(\Delta t^k)$, the value of the real Hamiltonian varies in the simulation only up to that order. $\Rightarrow$No energy drift.

## 4.4 Stability limit of the Verlet scheme for harmonic oscillators

- Despite the theoretical prediction that splitting schemes should be stable, one sees in practice that large time steps still lead to instabilities.

- To understand that, we will apply the splitting method to a harmonic oscillator.

- Hamiltonian of the harmonic oscillator:

  $$\mathcal{H} = \frac{1}{2}p^2 + \frac{1}{2}r^2$$

- Note: mass and frequency have been set to 1.
- Split the Hamiltonian in a kinetic part $K = \frac{1}{2}p^2$ and a potential part $U = \frac{1}{2}r^2$
- Use the Verlet scheme

$$e^{\mathcal{L}_{\mathcal{H}}\Delta t} = e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t} e^{\mathcal{L}_U \Delta t/2} + \mathcal{O}(\Delta t^3)$$

- Since $\mathcal{L}_K = (\mathsf{J} \cdot \frac{\partial K}{\partial \Gamma})^T \cdot \frac{\partial}{\partial \Gamma}$, one has

$$e^{\mathcal{L}_K \Delta t}\mathbf{x} = \begin{pmatrix} r + p\Delta t \\ p \end{pmatrix} = \begin{pmatrix} 1 & \Delta t \\ 0 & 1 \end{pmatrix} \cdot \mathbf{x},$$

  where

$$\mathbf{x} = \begin{pmatrix} r \\ p \end{pmatrix},$$

  so the operator $e^{\mathcal{L}_K \Delta t}$ acts as a linear operator.

- Similarly, $\mathcal{L}_U = (\mathsf{J} \cdot \frac{\partial U}{\partial \Gamma})^T \cdot \frac{\partial}{\partial \Gamma}$, and

$$e^{\frac{1}{2}\mathcal{L}_U \Delta t}\mathbf{x} = \begin{pmatrix} r \\ p - \frac{1}{2} r \Delta t \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ -\frac{1}{2}\Delta t & 1 \end{pmatrix} \cdot \mathbf{x}.$$

- Combining these linear operators in a single Verlet step gives

$$e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t} e^{\mathcal{L}_U \Delta t/2}\mathbf{x} = \begin{pmatrix} 1 - \frac{1}{2}\Delta t^2 & \Delta t \\ -\Delta t(1 - \frac{1}{4}\Delta t^2) & 1 - \frac{1}{2}\Delta t^2 \end{pmatrix} \cdot \mathbf{x}. \tag{4.39}$$

- We saw above that a splitting method conserves a pseudo-Hamiltonian, which is composed of the original Hamiltonian plus repeated Poisson brackets of the partial Hamiltonians.
- To leading order, we had

$$\mathcal{H}_{\text{pseudo}} = \mathcal{H} - \frac{1}{24}\{\{K, U\}, U\}\Delta t^2 + \frac{1}{12}\{\{U, K\}, K\}\Delta t^2 + \ldots$$

- Since $\{K, U\} = -pr$, one finds

$$\{\{K, U\}, U\} = r^2$$
$$\{\{U, K\}, K\} = p^2$$

- Thus, the first additional terms in the pseudo-Hamiltonian are of the same form as those in the Hamiltonian itself.
- Since higher order terms are repeated Poisson brackets, these too are of the same forms, so the full pseudo-Hamiltonian can be written as a renormalized harmonic oscillator Hamiltonian:

$$\mathcal{H}_{\text{pseudo}} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2,$$

  where $m$ and $\omega$ are a renormalized mass and a renormalized frequency.
- From the leading order terms in the pseudo Hamiltonian, we find

$$\omega = 1 + \frac{\Delta t^2}{24} + \mathcal{O}(\Delta t^4)$$
$$m = 1 - \frac{\Delta t^2}{6} + \mathcal{O}(\Delta t^4)$$

- As long as $m$ and $\omega^2$ are positive quantities, the scheme is stable, since a harmonic oscillator is stable.
- To test whether this is the case, we need to know all the correction terms.
- In this harmonic case, this can be done, as follows:
- We know the general form $\frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2$ of the Hamiltonian, which we write in matrix form

$$\mathcal{H}_{\text{pseudo}} = \mathbf{x}^T \cdot \mathsf{H} \cdot \mathbf{x}$$

  where

$$\mathsf{H} = \begin{pmatrix} \frac{1}{2m} & 0 \\ 0 & \frac{1}{2}m\omega^2 \end{pmatrix}.$$

- The resulting Liouvillean is then

$$\mathcal{L}_{\mathcal{H}_{\text{pseudo}}}\mathbf{x} = \left[\mathsf{J} \cdot \frac{\partial \mathcal{H}_{\text{pseudo}}}{\partial \mathbf{x}}\right]^T \frac{\partial}{\partial \mathbf{x}}\mathbf{x} = \mathsf{J} \cdot \frac{\partial \mathcal{H}_{\text{pseudo}}}{\partial \mathbf{x}} = \underbrace{2\mathsf{J} \cdot \mathsf{H}}_{\equiv \mathsf{L}} \cdot \mathbf{x},$$

  so the linear matrix corresponding to the Liouvillian is given by

$$\mathsf{L} = \begin{pmatrix} 0 & m\omega^2 \\ -\frac{1}{m} & 0 \end{pmatrix}$$

- The solutions of the equations of motion are determined by $e^{\mathrm{L}\Delta t}$, which is found to be

$$e^{\mathrm{L}\Delta t} = \begin{pmatrix} \cos(\omega\Delta t) & m\omega\sin(\omega\Delta t) \\ -\frac{1}{m\omega}\sin(\omega\Delta t) & \cos(\omega\Delta t) \end{pmatrix}$$

  This is not a surprising result, since it is just the solution of the classical harmonic oscillator.

- This result should coincide with the form on the right-hand side of equation (4.39).

- We can therefore identify the renormalized frequency and mass in the splitting scheme:

$$\omega = \frac{1}{\Delta t}\arccos(1 - \frac{1}{2}\Delta t^2) \tag{4.40}$$

$$m = \frac{\Delta t}{\omega\sin(\omega\Delta t)} \tag{4.41}$$

- Note that the arccos gives a real result for $\Delta t \leq 2$.

- For larger $\Delta t$, the arccos becomes imaginary, indicating that the scheme has become unstable.

- The way the instability limit is approached is illustrated in figure 4.1, where $\omega$ and $m$ are plotted as a function of $\Delta t$.

- We see that while the renormalized frequency remains finite up to the limit $\Delta t = 2$, the renormalized mass goes to infinity.

- This divergence shows that the pseudo Hamiltonian is not bounded.

- Only a bounded pseudo-Hamiltonian guarantees a stable algorithm.

- So an instability for large time steps arises even for the simple case of an harmonic oscillator

- The instability arises from an unbounded, diverging pseudo-Hamiltonian.

- Why could the pseudo-Hamiltonian diverge in the first place?

- Consider equation (4.38) again, which gives the pseudo-Hamiltonian as a power series in $\Delta t$.

- Generally, power series converge only if $\Delta t < \Delta t^*$, where $\Delta t^*$ is the radius of convergence.

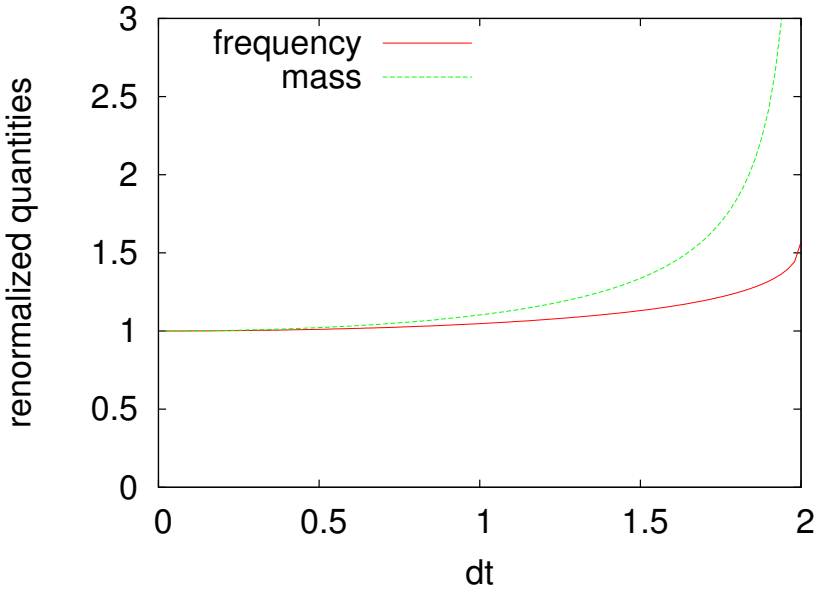



Figure 4.1: The way the instability limit is approached when using the Verlet splitting scheme on the harmonic oscillator. Plotted are the renormalized frequency $\omega$ and mass $m$ as a function of $\Delta t$. The unnormalized values were 1.

- For the harmonic oscillator, the radius of convergence was clearly $\Delta t^* = 2$.
- Also for general system, one expects a radius of convergence, i.e., a time step beyond which the pseudo-Hamiltonian becomes unbounded and the simulation becomes unstable.

## 4.5 More accurate splitting schemes

- Higher order schemes give better accuracy, but at the price of performing more force computations.
- Higher order schemes are very important in contexts such as astrophysics, where accurate trajectories matter.
- For MD, depending on the level of accuracy required, higher order schemes can also be advantageous.
- Higher order schemes may be devised by
  - taking time points which are not evenly spaced,

- incorporating leading order correction terms in the pseudo-Hamiltonian
- incorporating more time points,
- or a combination of the above.

All but the first option lead to more force computations per unit of physical time, which decreases the efficiency.

- We will restrict ourselves to symmetric splitting schemes, to ensure time-reversibility.
- To facilitate many of the derivations, we restate the symmetrized BCH formula of equation (4.34)

$$e^X e^Y e^X = e^{2X+Y-\frac{1}{6}[X,[X,Y]]+\frac{1}{6}[Y,[Y,X]]+\text{fifth repeated } X,Y \text{ commutators}}. \tag{4.42}$$

### 4.5.1 Optimized schemes

- Given the same Hamiltonian split-up

$$\mathcal{H} = K + U,$$
$$\mathcal{L} = \mathcal{L}_K + \mathcal{L}_U,$$

let us now explore a five-fold split up

$$e^{\mathcal{L}\Delta t} \approx e^{\eta\mathcal{L}_U\Delta t} e^{\mathcal{L}_K\Delta t/2} e^{(1-2\eta)\mathcal{L}_U\Delta t} e^{\mathcal{L}_K\Delta t/2} e^{\eta\mathcal{L}_U\Delta t}. \tag{4.43}$$

- Note that this is a case of uneven time-intervals.
- Work out the inner three exponentials using equation (4.42)

$$\begin{aligned}
&e^{\eta\mathcal{L}_U\Delta t} e^{\mathcal{L}_K\Delta t/2} e^{(1-2\eta)\mathcal{L}_U\Delta t} e^{\mathcal{L}_K\Delta t/2} e^{\eta\mathcal{L}_U\Delta t} \\
&= e^{\eta\mathcal{L}_U\Delta t} e^{\mathcal{L}_K\Delta t+(1-2\eta)\mathcal{L}_U\Delta t-\frac{(1-2\eta)\Delta t^3}{24}[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]+\frac{(1-2\eta)^2\Delta t^3}{12}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]]+\mathcal{O}(\Delta t^5)} e^{\eta\mathcal{L}_U\Delta t} \\
&= \exp\left\{ \mathcal{L}_K\Delta t + \mathcal{L}_U\Delta t - \frac{(1-2\eta)\Delta t^3}{24}[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]] + \frac{(1-2\eta)^2\Delta t^3}{12}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]] \right. \\
&\qquad \left. - \frac{\eta^2\Delta t^3}{6}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]] + \frac{\eta\Delta t^3}{6}[\mathcal{L}_K+(1-2\eta)\mathcal{L}_U,[\mathcal{L}_K,\mathcal{L}_U]] + \mathcal{O}(\Delta t^5) \right\} \\
&= e^{\mathcal{L}_\mathcal{H}\Delta t+\Delta t^3\left(\frac{6\eta-1}{24}[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]+\frac{1-6\eta+6\eta^2}{12}[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]]\right)+\mathcal{O}(\Delta t^5)} \\
&= e^{\mathcal{L}_\mathcal{H}\Delta t+\Delta t^3(\nu_1[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]+\nu_2[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]])+\mathcal{O}(\Delta t^5)}
\end{aligned}$$

where

$$\nu_1 = \frac{6\eta - 1}{24}$$
$$\nu_2 = \frac{1 - 6\eta + 6\eta^2}{12}$$

- If both $\nu_1$ and $\nu_2$ were zero, this would give a fourth order scheme.
  However, this is not possible here: we have one parameter and two prefactors to set to zero.

- Alternatively, one could make the error "as small as possible", e.g. by minimizing $\nu_1^2 + \nu_2^2$. This gives

$$\eta = 0.1931833275037836\ldots \tag{4.44}$$

- The scheme in equation (4.43) that uses this value of $\eta$ is called the Higher-order Optimized Advanced scheme of second order, or HOA2 for short.

- In general, optimized schemes are based on minimizing the formal error, but this cannot guarantee that the actual error is small: Numerical tests are necessary.

- The HOA2 scheme requires two force computations:

$$\underbrace{e^{\eta\mathcal{L}_U\Delta t}}_{\text{from previous step}} \quad e^{\mathcal{L}_K\Delta t/2} \quad \underbrace{e^{(1-2\eta)\mathcal{L}_U\Delta t}}_{\text{1st force computation}} \quad e^{\mathcal{L}_K\Delta t/2} \quad \underbrace{e^{\eta\mathcal{L}_U\Delta t}}_{\text{2nd force computation,}} \tag{4.45}$$

  whereas the Verlet scheme requires just one.

- Thus, to compare accuracies at fixed numerical cost, the time step should be taken twice as large in the HOA2 scheme as in the Verlet scheme.

- The HOA2 scheme was tested on a model of water (TIP4P) [Van Zon, Omelyan and Schofield, J. Chem. Phys **128**, 136102 (2008)], with the following results:

  - As long as it is stable, the HOA2 scheme leads to smaller fluctuations in the total energy than the Verlet scheme at the same computational cost.
  - In the water simulation, the HOA2 scheme becomes unstable for smaller time steps than the Verlet scheme.
  - The superior stability of the Verlet scheme means that it is the method of choice for quick and dirty simulations of water with an accuracy less than approximately 1.5% (as measured by the energy fluctuations).

  - For more accurate simulations, the HOA2 is more efficient, by about 50%, until the HOA2 scheme becomes unstable.

- The higher instability of HOA2 at large time steps, is due to the uneven time-steps than are taken.
- The average time step determines the computational cost, but the largest of the time steps determines the stability.
- Using uneven time steps instead of even time steps (at fixed computational cost) therefore increases some of the time intervals and decreases other.
- $\Rightarrow$ uneven time steps become unstable for smaller time steps than even time step variants.

### 4.5.2 Higher order schemes from more elaborate splittings

- While using the HOA2 scheme is beneficial, this could only be known after numerical tests.
- True higher-order schemes are a bit better in that respect: one knows that at least for small enough $\Delta t$, they are more efficient.
- The simplest way to get a higher order scheme is to concatenate lower order schemes.
- To understand this, note that if we have a $k$-th order scheme $S_k(\Delta t)$ approximating $S(\Delta t) = e^{\mathcal{L}\Delta}$ up to $\mathcal{O}(\Delta t^{k+1})$, i.e., if

$$S_k(\Delta t) = S(\Delta t) + \Delta t^{k+1}\delta S + \mathcal{O}(\Delta t^{k+3})$$

then

$$S_k(\Delta s)S_k(\Delta t - 2\Delta s)S_k(\Delta s) \tag{4.46}$$
$$= S(\Delta t) + \Big[2\Delta s^{k+1} + (\Delta t - 2\Delta s)^{k+1}\Big]\delta S + \mathcal{O}(\Delta t^{k+3}) \tag{4.47}$$

The leading order term can be eliminated by choosing

$$2\Delta s^{k+1} = -(\Delta t - 2\Delta s)^{k+1}, \tag{4.48}$$

which, if $k$ is even, can be solved and gives

$$\Delta s = \frac{\Delta t}{2 - 2^{1/(k+1)}}. \tag{4.49}$$

- When $S_k = S_2$ is given by the second Verlet scheme, the corresponding fourth order scheme becomes

$$\begin{aligned} e^{\mathcal{L}\Delta t} &\approx e^{\mathcal{L}_U \Delta s/2} e^{\mathcal{L}_K \Delta s} e^{\mathcal{L}_U \Delta s/2} e^{\mathcal{L}_U (\Delta t/2 - \Delta s)} e^{\mathcal{L}_K (\Delta t - 2\Delta s)} e^{\mathcal{L}_U (\Delta t/2 - \Delta s)} e^{\mathcal{L}_U \Delta s/2} e^{\mathcal{L}_K \Delta s} e^{\mathcal{L}_U \Delta s/2} \\ &= e^{\mathcal{L}_U \Delta s/2} e^{\mathcal{L}_K \Delta s} e^{\mathcal{L}_U (\Delta t - \Delta s)/2} e^{\mathcal{L}_K (\Delta t - 2\Delta s)} e^{\mathcal{L}_U (\Delta t - \Delta s)/2} e^{\mathcal{L}_K \Delta s} e^{\mathcal{L}_U \Delta s/2} \end{aligned} \tag{4.50}$$

  This is called the fourth order Forest-Ruth integration scheme (FR4). Note that it has seven parts and requires three force evaluations per time step.

- Note that $\Delta s > \Delta t/2$, so that $\Delta t - 2\Delta s < 0$.

- It therefore requires to take a negative time step:
  This tends to lead to instabilities.

- One can prove that order $k$ splitting schemes using a two-operator split up (such as $\mathcal{L}_U$ and $\mathcal{L}_K$) must have at least one negative time step if $k > 2$.

- The negative steps thus seem unavoidable.

- One can minimize these however, by allowing more general splitting schemes than those constructed from equation (4.46), i.e., using the general form in equation (4.32).

- This gives more parameters, allowing one to combine this with the higher-order nature with optimization, i.e. minimizing the leading error terms (cf. the HOA2 scheme).

- A good fourth order scheme of this type is called EFRL4 (Extended Forest-Ruth-like Fourth order scheme) and looks like this:

$$\begin{aligned} e^{\mathcal{L}\Delta t} = {} & e^{\mathcal{L}_U \xi \Delta t} e^{\mathcal{L}_K (\frac{1}{2} - \lambda)\Delta t} e^{\mathcal{L}_U \chi \Delta t} e^{\mathcal{L}_K \lambda \Delta t} e^{\mathcal{L}_U (1 - 2\chi - 2\xi)\Delta t} e^{\mathcal{L}_K \lambda \Delta t} e^{\mathcal{L}_U \chi \Delta t} e^{\mathcal{L}_K (\frac{1}{2} - \lambda)\Delta t} e^{\mathcal{L}_U \xi \Delta t} \\ & + \mathcal{O}(\Delta t^5), \end{aligned} \tag{4.51}$$

  where

$$\begin{aligned} \xi &= 0.3281827559886160 \\ \lambda &= 0.6563655119772320 \\ \chi &= -0.09372690852966102 \end{aligned}$$

  Even though this requires four force evaluations for each time step, it is more efficient than the FR4 scheme due to a much smaller leading order error.

### 4.5.3 Higher order schemes using gradients

- Gradients are, in this context, derivatives and higher-order derivatives of the potential.
- Using gradients as auxiliary Hamiltonians, one can reduce the order of a scheme
- The simplest can be derived by considering once more the five-fold splitting scheme, before optimization:

$$\begin{aligned} e^{\eta\mathcal{L}_U\Delta t}e^{\mathcal{L}_K\Delta t/2}e^{(1-2\eta)\mathcal{L}_U\Delta t}e^{\mathcal{L}_K\Delta t/2}e^{\eta\mathcal{L}_U\Delta t} &= e^{\mathcal{L}_{\mathcal{H}}\Delta t+\Delta t^3(\nu_1[\mathcal{L}_K,[\mathcal{L}_K,\mathcal{L}_U]]+\nu_2[\mathcal{L}_U,[\mathcal{L}_U,\mathcal{L}_K]])+\mathcal{O}(\Delta t^5)} \\ &= e^{\mathcal{L}_{\mathcal{H}}\Delta t+\Delta t^3\left(\nu_1\mathcal{L}_{\{\{U,K\},K\}}+\nu_2\mathcal{L}_{\{\{K,U\},U\}}\right)+\mathcal{O}(\Delta t^5)} \end{aligned}$$

  where

$$\begin{aligned} \nu_1 &= \frac{6\eta-1}{24} \\ \nu_2 &= \frac{1-6\eta+6\eta^2}{12} \end{aligned}$$

  and let $K$ and $U$ be of the usual form such that (cf. equations (4.35) and (4.36))

$$\begin{aligned} \{\{K,U\},U\} &= \frac{\partial U}{\partial R^N}\cdot\frac{\partial^2 K}{\partial P^N\partial P^N}\cdot\frac{\partial U}{\partial R^N} = \frac{1}{m}\left|\frac{\partial U}{\partial R^N}\right|^2 = \frac{1}{m}|F^N|^2 \\ \{\{U,K\},K\} &= \frac{\partial K}{\partial P^N}\cdot\frac{\partial^2 U}{\partial R^N\partial R^N}\cdot\frac{\partial K}{\partial P^N} = \frac{1}{m^2}P^N\cdot\frac{\partial^2 U}{\partial R^N\partial R^N}\cdot P^N. \end{aligned}$$

- The former depends only on $R^N$, but the latter is more complicated and depends on both $R^N$ and $P^N$.
- We can eliminate the more complicated term by setting $\nu_1 = 0 \Rightarrow \eta = 1/6$, leaving us with

$$\begin{aligned} e^{\frac{1}{6}\mathcal{L}_U\Delta t}e^{\frac{1}{2}\mathcal{L}_K\Delta t}e^{\frac{2}{3}\mathcal{L}_U\Delta t}e^{\frac{1}{2}\mathcal{L}_K\Delta t}e^{\frac{1}{6}\mathcal{L}_U\Delta t} &= e^{\mathcal{L}_{\mathcal{H}}\Delta t+\Delta t^3\frac{1}{72m}\mathcal{L}_{|F^N|^2}+\mathcal{O}(\Delta t^5)} \\ &= e^{\left[\mathcal{L}_K+\mathcal{L}_{U+\frac{\Delta t^2}{72m}|F^N|^2}\right]\Delta t+\mathcal{O}(\Delta t^5)} \end{aligned}$$

- This equation holds for any form of $U$!
- Thus we may substitute for $U$ the expression

$$\tilde{U} = U - \frac{\Delta t^2}{72m}\left|F^N\right|^2, \tag{4.52}$$

giving

$$e^{\frac{1}{6}\mathcal{L}_{\tilde{U}}\Delta t}e^{\frac{1}{2}\mathcal{L}_K\Delta t}e^{\frac{2}{3}\mathcal{L}_{\tilde{U}}\Delta t}e^{\frac{1}{2}\mathcal{L}_K\Delta t}e^{\frac{1}{6}\mathcal{L}_{\tilde{U}}\Delta t} = e^{\left[\mathcal{L}_K+\mathcal{L}_{\tilde{U}+\frac{\Delta t^2}{72m}|F^N|^2}\right]\Delta t+\mathcal{O}(\Delta t^5)}$$
$$= e^{[\mathcal{L}_K+\mathcal{L}_U]\Delta t+\mathcal{O}(\Delta t^5)} = e^{\mathcal{L}_{\mathcal{H}}\Delta t+\mathcal{O}(\Delta t^5)}$$

A fourth order integration scheme!

- Note that no negative time steps were needed.
- The scheme in the current form uses an effective potential $\tilde{U}$, which differs from the real potential $U$ by an additional term $\delta U = -\frac{\Delta t^2}{72m}\left|F^N\right|^2$ of order $\mathcal{O}(\Delta t^2)$. To leading order, this term commutes with all factors, so one may also write

$$\begin{aligned} e^{\mathcal{L}_{\mathcal{H}}\Delta t+\mathcal{O}(\Delta t^5)} &= e^{\frac{1}{6}\mathcal{L}_U\Delta t}e^{\frac{1}{2}\mathcal{L}_K\Delta t}e^{\frac{2}{3}\mathcal{L}_U\Delta t+\delta U\Delta t}e^{\frac{1}{2}\mathcal{L}_K\Delta t}e^{\frac{1}{6}\mathcal{L}_U\Delta t} \\ &= e^{\frac{1}{6}\mathcal{L}_U\Delta t}e^{\frac{1}{2}\mathcal{L}_K\Delta t}e^{\frac{2}{3}[\mathcal{L}_U+\frac{3}{2}\delta U]\Delta t}e^{\frac{1}{2}\mathcal{L}_K\Delta t}e^{\frac{1}{6}\mathcal{L}_U\Delta t} \\ &= e^{\frac{1}{6}\mathcal{L}_U\Delta t}e^{\frac{1}{2}\mathcal{L}_K\Delta t}e^{\frac{2}{3}[\mathcal{L}_{\tilde{\tilde{U}}}]\Delta t}e^{\frac{1}{2}\mathcal{L}_K\Delta t}e^{\frac{1}{6}\mathcal{L}_U\Delta t} \end{aligned} \tag{4.53}$$

where the modified potential in the middle step is

$$\tilde{\tilde{U}} = U + \frac{3}{2}\delta U = U - \frac{\Delta t^2}{48m}\left|F^N\right|^2. \tag{4.54}$$

- Scheme (4.53) is due to Suzuki.
- To summarize: by taking uneven intervals and incorporating the correction terms (using gradients of the potentials), we get a fourth order scheme which does not require negative partial steps and only needs two force evaluations per step.
- Note that to be able to use the modified potentials, the forces have to be well defined, i.e., any cut-off has to be smooth enough.

### 4.5.4 Multiple time-step algorithms

- Decompose the potential and the corresponding Liouville operator into two parts: one for fast varying forces and the other for the slow varying forces:

$$U = U_{\mathrm{f}} + U_{\mathrm{s}} \tag{4.55}$$

- The fast motion could represent e.g. , intermolecular vibrations while the slowly varying forces might be intermolecular forces.

- The simplest multiple time-step algorithm is then

$$e^{\frac{1}{2}\mathcal{L}_{U_\mathrm{s}}\Delta t}\left(e^{\frac{1}{2}\mathcal{L}_{U_\mathrm{f}}\Delta t/M}e^{\mathcal{L}_K\Delta t/M}e^{\frac{1}{2}\mathcal{L}_{U_\mathrm{f}}\Delta t/M}\right)^M e^{\frac{1}{2}\mathcal{L}_{U_\mathrm{s}}\Delta t} = e^{\mathcal{L}\Delta t+\mathcal{O}(\Delta t^3)}. \tag{4.56}$$

- While this is of second order, like the Verlet scheme, the time step for the fast part of the motion if $M$ times smaller than that of the slow motion.