

Molecular dynamics simulation

how to get things moving

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Motivation

Consider a (bio)molecule in aqueous solution
at ambient conditions

- structure is varying
- interactions are varying (H-bonds)
- the energy of the system is fluctuating
- description with a single, static structure – meaningless
- an interesting process may be going on 😊
- then, multiple 'structures' may be relevant

State of the system

(micro)state of a system:

positions \vec{r}_i and momenta \vec{p}_i of all the particles (atoms)

configuration space – $3N$ -dimensional space of coordinates

phase space – $6N$ -dim. space of coords and momenta $\{\vec{r}_i, \vec{p}_i\}$

trajectory in phase space – sequence of points $\{\vec{r}_i(t), \vec{p}_i(t)\}$
passed by the system in course of time

State of the system

Example – 1D harmonic oscillator:
time course of coordinate and of velocity

$$r(t) = a \cdot \cos[\omega t]$$

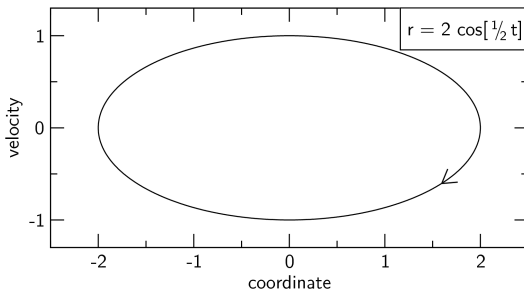
$$v(t) = -a\omega \cdot \sin[\omega t]$$

plot of velocity vs. coordinate – in 2D phase space:
elliptic trajectory

$$\left(\frac{x(t)}{a}\right)^2 + \left(\frac{v(t)}{a \cdot \omega}\right)^2 = 1$$

State of the system

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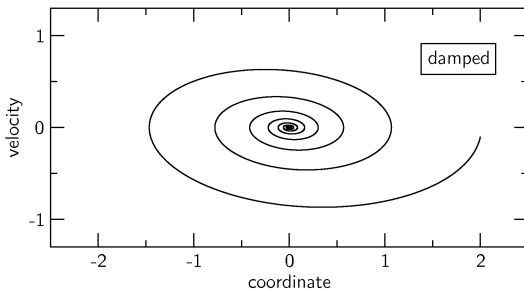


$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{pot}} = \frac{1}{2} m \omega^2 a^2$$

conservative system – total energy remains conserved (constant)

State of the system

Example – 1D harmonic oscillator:



with **friction** or other **damping** – system is losing energy,

Thermodynamic properties

Back to the **molecule in solution**:

MD simulation – we generate a trajectory in phase space

for some time \rightarrow **snapshots** $\{\vec{r}_i(t_k), \vec{p}_i(t_k)\}$,

evaluate energy in time instants t_k ($k = 1, \dots, M$) $\rightarrow E_k$

and calculate the average:

$$\langle E \rangle_t = \frac{1}{M} \sum_{k=1}^M E_k$$

generally – we obtain the average value of the property of interest,
over all observed structures

to obtain the change of the property in a **reaction**:

we do this for the product and for the reactant,

obtain averages for both states and subtract them

Thermodynamic properties

we obtain the trajectory by doing an MD simulation

– a good idea, but still there are issues:

- Do we have enough snapshots? – all relevant conformations?

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- Suppose we know the structure of the reactant.
How do we get the structure of the product?
or even the whole reaction path?

Thermodynamic properties

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- Do we have enough snapshots? – all relevant conformations?
- How do we consider experimental conditions – temperature?
- Suppose we know the structure of the reactant.
How do we get the structure of the product?
or even the whole reaction path?
- Does the average of energy provide useful information?
What about free energies / entropy?

Thermodynamic properties

Characteristics of (bio)molecular simulations:

- it is easy to derive the total energy – force field
- not so easy to make proper use of the energy function
to get the **thermodynamic properties** right
- it is all about thermodynamics
in possible contrast to quantum chemistry

Thermodynamic properties

time average for energy and other properties of interest:

$$\langle A \rangle_t = \frac{1}{t_1 - t_0} \int_{t_0}^{t_1} A(t) dt$$

experimental sample – huge number of molecules,
all relevant conformations of molecule/solvent are present
– thermodynamic **ensemble**

How many molecules in the ensemble are found in $\{\vec{r}_i, \vec{p}_i\}$?

→ **phase-space density** (per volume unit) $\rho(\vec{r}, \vec{p})$

→ **ensemble average** can be calculated:

$$\langle A \rangle_e = \frac{\int A \cdot \rho(\vec{r}, \vec{p}) d\vec{r} d\vec{p}}{\int \rho(\vec{r}, \vec{p}) d\vec{r} d\vec{p}}$$

Thermodynamic properties

experiment – ensemble average is always measured

simulation – a single molecule – time average available

simulation – system is considered **ergodic**

- passes through all points of phase space

- constituting the real ensemble

- provided the simulation is long enough

- implies:

$$\langle A \rangle_t = \langle A \rangle_e$$

the topic of **sampling**, danger of undersampling

Dèjà vu

the total energy of a typical biomolecular force field:

$$\begin{aligned}
 E(R^N) = & \\
 = & \frac{1}{2} \sum_i k_i (r_i - r_i^0)^2 + \frac{1}{2} \sum_j k_j^\vartheta (\vartheta_j - \vartheta_j^0)^2 + \frac{1}{2} \sum_n V_n \cdot \cos[n\omega - \gamma_n] \\
 + & \sum_i^N \sum_{j=i+1}^N \left\{ 4\varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right) + \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} \right\}
 \end{aligned}$$

Dèjà vu

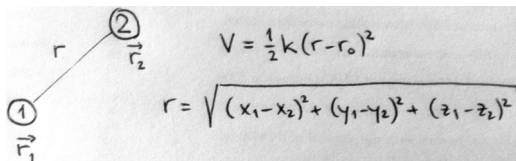
force acting on atom i

– derivative of energy with respect to the coordinates of atom i

$$\begin{aligned}\vec{F}_i &= -\nabla_i V \\ F_i^x &= -\frac{\partial V}{\partial x_i}\end{aligned}$$

derivatives of all of the terms in the force field
are obtained in an analytical form easily

Dèja vu



$$\frac{\partial r}{\partial x_1} = \frac{1}{2} \cdot \frac{1}{r} \cdot \frac{\partial (x_1 - x_2)^2}{\partial x_1} = \frac{1}{2r} \cdot 2(x_1 - x_2) = \frac{x_1 - x_2}{r}$$

$$\frac{\partial V}{\partial x_1} = \frac{1}{2} k \cdot 2(r - r_0) \cdot \frac{\partial r}{\partial x_1} = \frac{1}{2} k \cdot 2(r - r_0) \cdot \frac{x_1 - x_2}{r} =$$

$$= k \cdot (r - r_0) \cdot \frac{x_1 - x_2}{r}$$

$$\nabla_1 V = k \cdot (r - r_0) \cdot \frac{\vec{r}_1 - \vec{r}_2}{r}$$

$$\vec{F}_1 = -\nabla_1 V = k \cdot (r - r_0) \cdot \frac{\vec{r}_2 - \vec{r}_1}{r}$$

Equations of motion

total energy – **Hamilton function** (Hamiltonian):

$$H = T + V = \frac{1}{2} \frac{p^2}{m} + \frac{1}{2} k r^2$$

equations of motion in Hamilton's formalism:

$$\dot{r}_i = \frac{\partial H}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H}{\partial r_i}$$

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leading to **ordinary differential eqn** (ODE) of 2nd order

$$\dot{r} = \frac{\partial H}{\partial p} = \frac{p}{m} \rightarrow p = m\dot{r} \rightarrow \dot{p} = m \cdot \ddot{r}$$

$$\dot{p} = -\frac{\partial H}{\partial r} = -\frac{\partial V}{\partial r} = F$$

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$$m \cdot \ddot{r} = F$$

Equations of motion

example for harmonic oscillator (momentum $p = m \cdot v$):

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

$$\dot{r} = \frac{\partial H}{\partial p} = \frac{p}{m}$$

$$\dot{p} = -\frac{\partial H}{\partial r} = F = -k \cdot r$$

equation of motion:

$$m \cdot \ddot{r} = -k \cdot r$$

Relevant differential equations

1st-order ODE

- generally: $\dot{x} = f(x, t)$
- example: $\dot{x} = -k \cdot x$
- solution: $x(t) = A \cdot \exp[-k \cdot t]$
- e.g. radioactive decay, dynamics of populations

Relevant differential equations

2nd-order ODE:

- $\ddot{x} = f(x, \dot{x}, t)$
- example: eqn of motion of harmonic oscillator $\ddot{x} = -\frac{k}{m} \cdot x$
- with linear damping: $\ddot{x} = -\zeta \cdot \dot{x} - \frac{k}{m} \cdot x$
- reduction of 2nd-order ODE to **two** 1st-order ODEs
by introducing velocity v :

$$\begin{aligned}\dot{x} &= v \\ \dot{v} &= -\zeta \cdot v - \frac{k}{m} \cdot x\end{aligned}$$

these ODEs have to be solved numerically

(Too) simple numerical solution

$$\dot{r} = f(r, t)$$

common trick – Taylor expansion ($\Delta t = t - t_0$):

$$r(t) = r(t_0) + \dot{r}(t_0) \cdot \Delta t + \frac{1}{2} \ddot{r}(t_0) \cdot \Delta t^2 + \dots$$

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Euler method – 1st-order approximation:

$$r(t) \approx r(t_0) + \dot{r}(t_0) \cdot \Delta t$$

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Numerical integration starts at time t_0 – we make a **step Δt** :

$$a(t_0) = -\frac{F}{m}$$

$$r(t_0 + \Delta t) = r(t_0) + v(t_0) \cdot \Delta t$$

$$v(t_0 + \Delta t) = v(t_0) + a(t_0) \cdot \Delta t$$

Verlet – normal form

Euler method – too large numerical error $\mathcal{O}(\Delta t^2)$
more accurate integration is needed

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Verlet method:

Taylor expansion up to 2nd order,

derivation from two virtual steps, forwards and backwards:

$$r(t + \Delta t) = r(t) + \dot{r}(t) \cdot \Delta t + \frac{1}{2} \ddot{r}(t) \cdot \Delta t^2$$

$$r(t - \Delta t) = r(t) - \dot{r}(t) \cdot \Delta t + \frac{1}{2} \ddot{r}(t) \cdot \Delta t^2$$

Verlet – normal form

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add both equations – eliminate the velocity \dot{r} :

$$r(t + \Delta t) = 2 \cdot r(t) - r(t - \Delta t) + \ddot{r}(t) \Delta t^2$$

$$\ddot{r}(t) = a(t) = \frac{F(t)}{m} = -\frac{1}{m} \frac{\partial V}{\partial r}(t)$$

Verlet – normal form

$$r(t + \Delta t) = 2 \cdot r(t) - r(t - \Delta t) + \ddot{r}(t)\Delta t^2$$

strange – not only $r(t)$ and $a(t)$ needed, but also $r(t - \Delta t)$?

no problem – information equivalent to velocity, so that
initial conditions may be converted:

$$r(t_0 - \Delta t) = r(t_0) - v(t_0) \cdot \Delta t$$

velocities – not in there explicitly, but may be obtained:

$$\dot{r}(t) = v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2 \cdot \Delta t}$$

(Verlet normal form)

Verlet – normal form

program for 'astronomic' simulations: ($\vec{F} = -1/r^2 \cdot \vec{r}/r$)

```

/* initial "old" positions from initial velocities */
for (k=0; k<DIM; k++)
    r_old[k] = r[k] - v[k] * dt;

for (t=0.; t < CYCLES*PERIOD; t+=dt) {
    /* distance (from the Sun) */
    rnorm = sqrt(NORM2(r));
    /* gravitation force (on the comet)
    * f = -1 / r^2
    * multiply this by the unit vector in the direction of r
    * f = -1 / r^2 * vector(r) / r
    */
    for (k=0; k<DIM; k++)
        f[k] = - r[k] / CUB(rnorm);
    /* Verlet integrator */
    for (k=0; k<DIM; k++) {
        r_new = 2 * r[k] - r_old[k] + f[k] * SQR(dt);
        r_old[k] = r[k];
        r[k] = r_new;
    }
}

```

velocity Verlet

another, equivalent formulation

- positions calculated first using velocities

$$r(t + \Delta t) = r(t) + v(t) \cdot \Delta t + \frac{1}{2}a(t) \cdot \Delta t^2$$

- forces (\rightarrow accelerations) calculated in new positions, and new velocities obtained as

$$v(t + \Delta t) = v(t) + \frac{1}{2}(a(t) + a(t + \Delta t)) \cdot \Delta t$$

- next calculation of positions $r \dots$

MD is started with the knowledge of r_0 and v_0

in every step, $r(t + \Delta t)$ is calculated first

so that $a(t + \Delta t)$ can be updated, to get $v(t + \Delta t)$

velocity Verlet

VV – better numerical precision than normal Verlet
numerical problem of normal Verlet

- adding a small but important term $\ddot{r}(t_0)\Delta t^2$
to a large term calculated as difference: $2r(t) - r(t - \Delta t)$
- large relative uncertainty

desirable – use an algorithm that is mathematically equivalent but
does not require to perform potentially problematic calculations

Leap-frog

yet another equivalent formulation, similar to VV

– r and v are evaluated in an alternating fashion:

$r(t)$, $v(t + \frac{1}{2}\Delta t)$, $r(t + \Delta t)$, $v(t + \frac{3}{2}\Delta t)$, $r(t + 2\Delta t)$...

■ velocities at $t + \frac{1}{2}\Delta t$ are obtained first:

$$v(t + \frac{1}{2}\Delta t) = v(t - \frac{1}{2}\Delta t) + a(t) \cdot \Delta t$$

■ then, positions are updated at $t + \Delta t$:

$$r(t + \Delta t) = r(t) + v(t + \frac{1}{2}\Delta t) \cdot \Delta t$$

So, accelerations have to be calculated at t , $t + \Delta t$, $t + 2\Delta t$...

from forces, and positions are needed to compute forces

– in fact positions have to be known at the same t that we need a

Initial conditions

To start the MD

- the positions r_0 and the velocities v_0 have to be specified

First step – calculations of forces at r_0 to get accelerations a_0

Then – the integrator may provide r (and v) at time $t_0 + \Delta t$

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To obtain a trajectory over a time interval T ,

we perform M steps

- we have to evaluate the forces on all atoms $M = T/\Delta t$ times

Computational cost of the calculation of forces

determines how many steps we can afford to make

Δt – crucial parameter

Numerical issue:

- we neglect contributions in Δt^3 and higher orders \rightarrow error per step in the order of Δt^3 ($\mathcal{O}(\Delta t^3)$)
- keep the step short \rightarrow make the error small
- disadvantage: we may need too many steps to simulate certain time T
- trade-off: Δt too long \rightarrow too large error
dynamics may deviate, momentum may not be conserved. . .

Δt – crucial parameter

Chemical issue:

- fastest motion – hydrogen atoms, period around 10 fs
- rule of thumb – stable integration with $\Delta t \leq$ fastest period (much more relaxed than in ‘astronomic’ simulations ☺)
- practically, Δt of 1 fs is used (2 fs with special treatment)

→ 1M calculations of forces needed for a trajectory of 1 ns
large systems – multi-ns simulations routinely, μ s possible

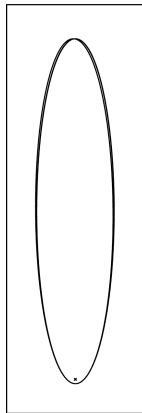
Δt – astronomic test

static heavy object (star) + moving light object (comet)
+ gravity ($F = -1/r^2$) → dynamics with Verlet integrator
gravity – inverse-square law much like Coulomb between atoms
exact trajectory – periodic along an ellipse with star in 1 focus

simulation – four different values of the time step:
 1×10^{-5} , 2×10^{-5} , 5×10^{-5} and 10×10^{-5} of the orbital period
→ 100k, 50k, 20k and 10k steps per period – mmore than in MD

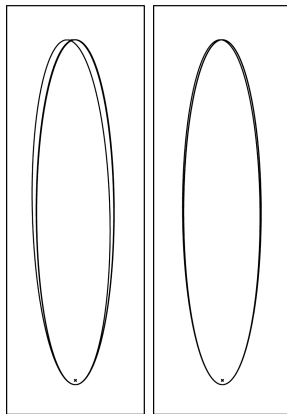
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first 10 orbits are shown, and then the 100th shown again



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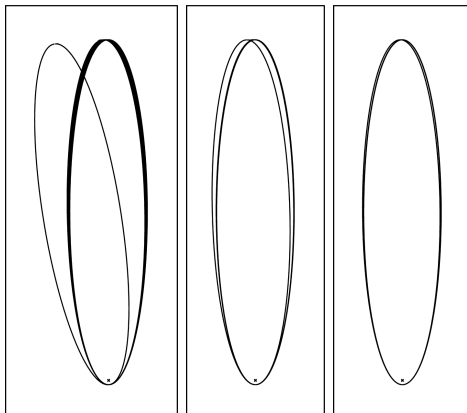
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credit for the idea: Jiří Kolafa, Prague

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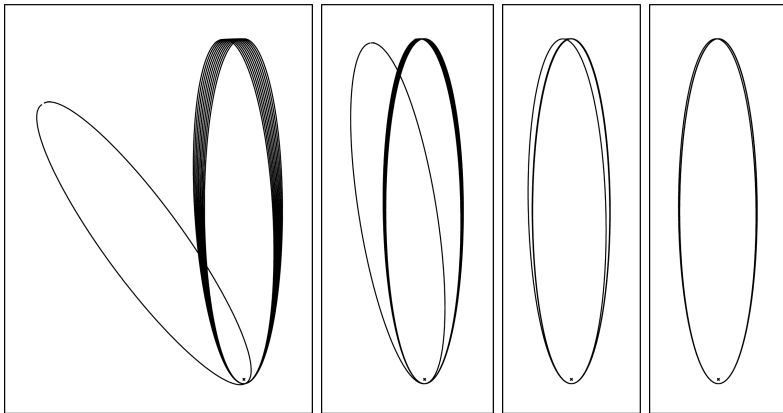
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Δt – astronomic test

shortest step – reasonable trajectory, small deviation

2nd-longest step – error becomes evident

longest step – large deviation

important – trajectory is precessing (ellipse is ‘rotating’),

but it remains elliptic whatever the time step is

constant remain also **total energy** and **orbital period**

– consequence of **reversibility** of Verlet:

if we reverse the course of time ($\Delta t \rightarrow -\Delta t$),

we will simulate towards initial conditions of the trajectory

generally – energy in Verlet fluctuates (with longer step),

but it does not **drift**

Verlet or something better?

Verlet – very approximative yet still routinely used for MD
why? – because it is efficient – why?

- forces on atoms (\rightarrow accelerations) calculated only $1\times$ per step
- no higher derivatives of positions are involved

more accurate methods to integrate ODEs are available, and are used in some applications, if improved accuracy is required

straightforward – involve extra terms from Taylor expansion
– hardly ever done, there are other ways to improve accuracy...

Gear: predictor–corrector

- provides solution correct to an order of choice
- new positions etc. are calculated (**predicted**) from the Taylor expansion using certain number of previous steps
- then, forces are calculated in the predicted positions → accelerations
- accelerations used to make **correction** of positions
- additional computational effort, decreased efficiency
- accuracy may be improved significantly, longer step possible
- still, only 1 calculation of forces per step

Gear: predictor–corrector

n th-order Gear integrator:

coords of all atoms \vec{r} and their derivatives up to the order of $n - 1$:

$$R = \begin{pmatrix} \vec{r} \\ \dot{\vec{r}} \cdot \Delta t \\ \ddot{\vec{r}} \cdot \frac{1}{2} \Delta t^2 \\ \dddot{\vec{r}} \cdot \frac{1}{6} \Delta t^3 \end{pmatrix}$$

for the 4th-order method

higher-order methods: derivatives come in as $\frac{d^k \vec{r}}{dt^k} \cdot \frac{1}{k!} \Delta t^k$

initialization: \vec{r} and $\dot{\vec{r}}$ from init. conditions, $\ddot{\vec{r}}$ calculated from forces
 – 1 calculation of forces required at start

higher derivatives may be set to zero

Gear: 1: prediction

MD step at time t starts with **prediction**
of coordinates+derivatives at time $t + \Delta t$:

$$R_p(t + \Delta t) = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 0 & 1 & 2 & 3 \\ 0 & 0 & 1 & 3 \\ 0 & 0 & 0 & 1 \end{pmatrix} \cdot R(t)$$

- the matrix contains binomial coefficients
- the calculation passes a polynomial of order $n - 1$
through the previous n points of the trajectory
(at $t, t - \Delta t, \dots t - (n - 1)\Delta t$)
and generates a point on this polynomial after Δt
- prediction may be good for continuous force functions
- no calculation of force up to this point!

Gear: 2: error

next, we calculate the **error** of the prediction:

we obtain the force at the predicted position,

and compare it with the force predicted in step 1 → error

$$E = \frac{1}{2} \left(\frac{\vec{f}(\vec{r}_p)}{m} - \ddot{\vec{r}}_p \right) \Delta t^2$$

E – vector with as many components as the vector of coordinates
(every coordinate with its derivatives has ‘its own’ error)

Gear: 3: correction

Finally, using the error E , we calculate the **corrected** coordinates and derivatives as

$$R(t + \Delta t) = R_p(t + \Delta t) + E \cdot \begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

coefficients $a_0, a_1 \dots a_{n-1}$

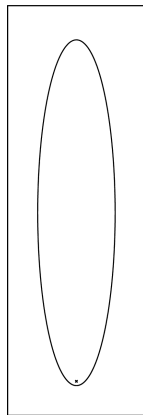
- estimated to prevent the accumulation of integration errors
- may be looked up in tables
- for 4th-order method for 2nd-order ODE, forces not depending on velocities: $a_0 = \frac{1}{6}, a_1 = \frac{5}{6}, a_2 = 1$ and $a_3 = \frac{1}{3}$

Gear – astronomic test

$\Delta t = 10 \times 10^{-5}, 5 \times 10^{-5}, 2 \times 10^{-5}$ and 1×10^{-5} of correct period

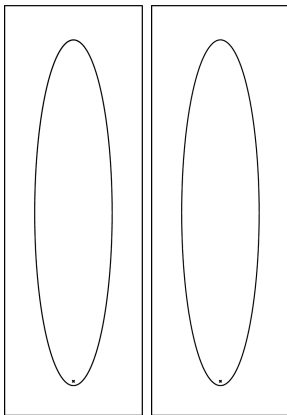
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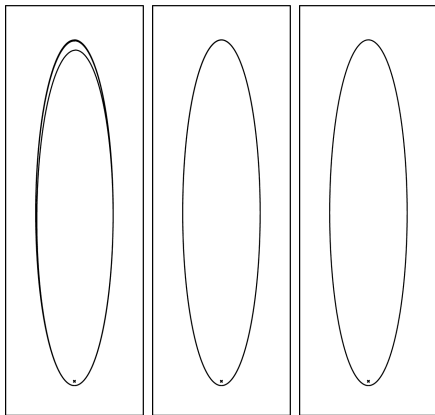
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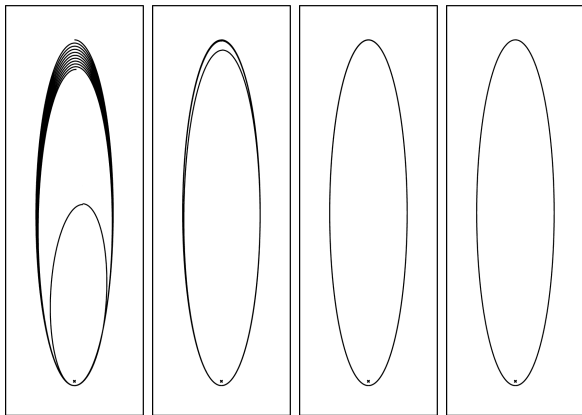
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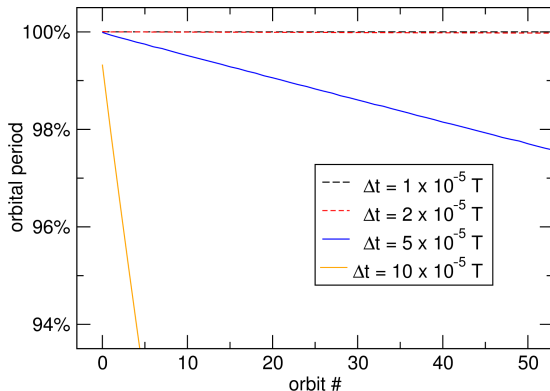
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Gear – astronomic test

- Gear may provide more accurate trajectories than Verlet, with the same Δt
- perfect trajectories with the two shortest time steps (Verlet showed deviations even with the shortest step)
- incorrect behavior with the second-largest step, just wrong with the longest one
- different **character of deviation** than with Verlet: the elliptic trajectory of the comet is getting 'shorter', rather than precessing
- important: the orbital **period** is becoming shorter, and total **energy is decreasing**

Gear – astronomic test



general observation:

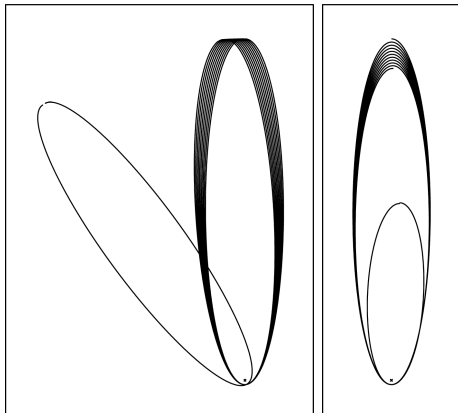
energy will decrease or increase (**drift**) in the simulation

this may be negligible with longer step / higher-order Gear

Gear: **not** reversible, does **not** conserve energy.

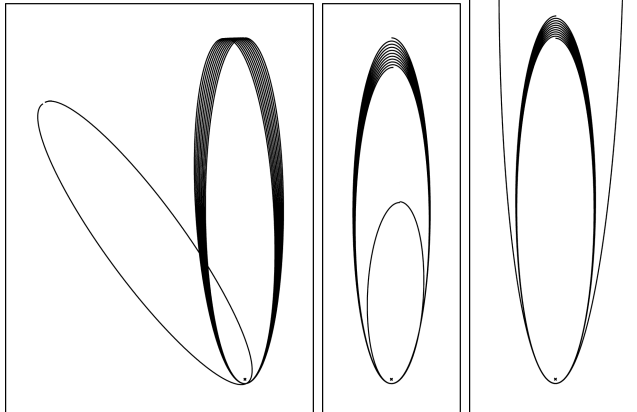
Gear – higher order?

Verlet and Gear 4th, 5th and 6th order ($\Delta t = 10 \times 10^{-5} T$)



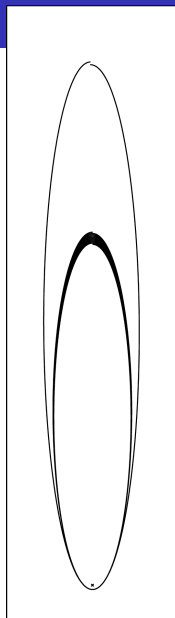
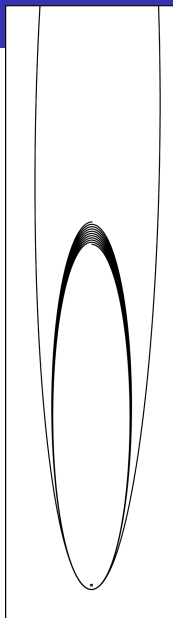
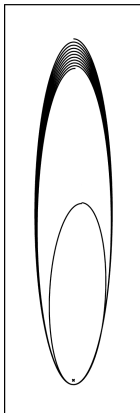
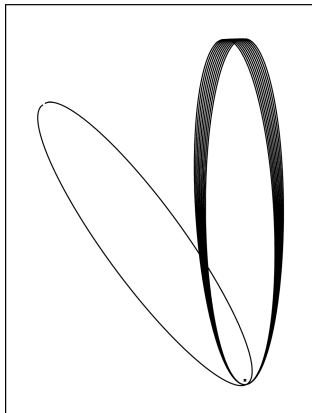
Gear – higher order?

Verlet and Gear 4th, 5th and 6th order ($\Delta t = 10 \times 10^{-5} T$)



Gear – higher order?

Verlet and Gear 4th, 5th and 6th order ($\Delta t = 10 \times 10^{-5} T$)



Gear – higher order?

note: Verlet corresponds to 3th-order Gear formally
higher derivatives in calculation improve the results only slightly
– the drift of energy is slower but still unsatisfactory

general observations:

- when making the step shorter,
results of higher-order methods will improve faster
- when making the time step longer,
higher-order methods are more prone to fail completely
while lower-order methods are more robust
- higher-order integrators are a good choice
if accurate trajectories are desired
- lower-order or Verlet integration is sufficient for applications
with 'weaker' requirements – typically, MD

Runge–Kutta integration

Runge–Kutta methods – numerical integrators of 1st-order ODEs
classical 4th-order method **RK4**:

- 4 calculations of the derivative in every step
- points at which the derivative is calculated
 - chosen depending on the previous calculations,
 - the first is done at the start of the integration step

$$g_0 = \dot{r}(r(t))$$

$$g_1 = \dot{r}\left(r(t) + \frac{1}{2}g_0\Delta t\right)$$

$$g_2 = \dot{r}\left(r(t) + \frac{1}{2}g_1\Delta t\right)$$

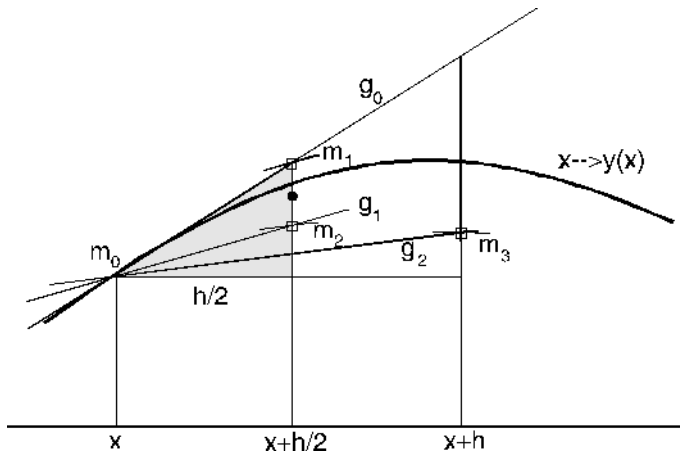
$$g_3 = \dot{r}\left(r(t) + g_2\Delta t\right)$$

We calculate the value of the function at time $t + \Delta t$
using a weighted average of the obtained derivative values:

$$r_{n+1} = r_n + \frac{1}{6}(g_0 + 2g_1 + 2g_2 + g_3) \cdot \Delta t$$

the RK4 method

derivative of y is calculated at points m_0 , m_1 , m_2 and m_3
calculated derivatives g_0, \dots, g_3 are shown as arrows



the RK4 method

- actually predictor–corrector with 4 predictions per step
- 4 calculations of the derivative needed per step
- error per step reduced to $\mathcal{O}(\Delta t^5)$ – 4th-order method
- solves 1st-order ODEs much like the Euler method does
- to solve Newton eqns of motion (2nd-order ODEs)
 - eqns are converted to system of two 1st-order eqns
 - positions and velocities of atoms are propagated:

$$\begin{aligned}\dot{\vec{r}} &= \vec{v} \\ \dot{\vec{v}} &= \frac{\vec{f}}{m}\end{aligned}$$

the RK4 method

Can RK4 be used directly somewhere in computational chemistry?

Yes! Let us propagate a time-dependent Schrödinger equation

– 1st-order ODE for the wave function Ψ of the system:

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} \hat{H} \Psi$$

- we express Ψ as linear combination of suitable basis functions:

$$\Psi = \sum_m c_m \varphi_m$$

- Hamiltonian is a matrix of elements between basis functions:

$$H_{mn} = \langle \varphi_m | \hat{H} | \varphi_n \rangle$$

- we calculate the derivative with matrix multiplication as $H \cdot \Psi$