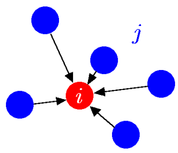
Molecular dynamics

- hard spheres etc. – collisions
- “classical” MD – integration of the equations of motion
- Brownian (stochastic) dynamics, dissipative particle dynamics = MD + random forces

Forces are needed:

$$\vec f_i = -\frac{\partial U(\vec r^N)}{\partial \vec r_i} \qquad i = 1,\dots,N$$



Example – pair forces:

$$U = \sum_{i<j} u(r_{ij}) \quad \Rightarrow \quad \vec f_i = \sum_{\substack{j=1\\ j\ne i}}^{N} \vec f_{ji} \equiv -\sum_{\substack{j=1\\ j\ne i}}^{N} \frac{\mathrm{d}u(r_{ji})}{\mathrm{d}r_{ji}} \frac{\partial r_{ji}}{\partial \vec r_i} = -\sum_{\substack{j=1\\ j\ne i}}^{N} \frac{\mathrm{d}u(r_{ji})}{\mathrm{d}r_{ji}} \frac{\vec r_{ji}}{r_{ji}}$$

Notation: $\vec r_{ij} = \vec r_j - \vec r_i$, $r_{ij} = |\vec r_{ij}|$

Newton’s equations of motion

$$\frac{\mathrm{d}^2 \vec r_i}{\mathrm{d}t^2} = \ddot{\vec r}_i = \frac{\vec f_i}{m_i}, \qquad i = 1,\dots,N$$

Method of finite differences, timestep h

Initial value problem: $\vec r$ and $\dot{\vec r}$ at time t_0 are known

Methods:

- Runge–Kutta: many evaluations of the right-hand side/step (costly!)
- Predictor–corrector: a bit better, Gear’s versions occasionally used (see below)
- Verlet and clones (symplectic = good energy conservation)
- Multiple timestep methods: more timescales (usually symplectic)
- Geometric integrators (symplectic)

Verlet method

Taylor expansion:

$$\begin{aligned} \vec r_i(t-h) &= \vec r_i(t) - h\dot{\vec r}_i(t) + \frac{h^2}{2}\ddot{\vec r}_i(t) - \dots & +1\times \\ \vec r_i(t) &= \vec r_i(t) & -2\times \\ \vec r_i(t+h) &= \vec r_i(t) + h\dot{\vec r}_i(t) + \frac{h^2}{2}\ddot{\vec r}_i(t) + \dots & +1\times \end{aligned}$$

$\Rightarrow$ numeric 2nd derivative: $\ddot{\vec r}_i(t) = \dfrac{\vec f_i(t)}{m_i} = \dfrac{\vec r_i(t-h) - 2\vec r_i(t) + \vec r_i(t+h)}{h^2} + \mathcal{O}(h^2)$

Verlet method: $\vec r_i(t+h) = 2\vec r_i(t) - \vec r_i(t-h) + h^2 \dfrac{\vec f_i(t)}{m_i}$

Initial values: $\vec r_i(t_0 - h) = \vec r_i(t_0) - h\dot{\vec r}_i(t_0) + \dfrac{h^2}{2}\dfrac{\vec f_i(t_0)}{m_i} + \mathcal{O}(h^3)$

- ⊕ time-reversible ($\Rightarrow$ no energy drift); even symplectic
- ⊖ cannot use for $\ddot r = f(r, \dot r)$ because $\dot r(t)$ is not known at time t

Identical trajectories: leap-frog, velocity Verlet, Gear ($m = 3$), Beeman

Leap-frog

velocity = displacement (change in position) per unit time h (vector)

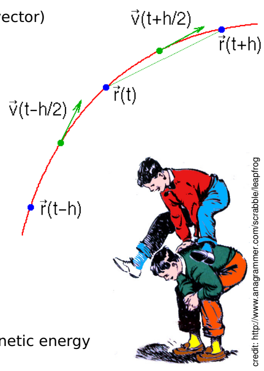
$$\vec v(t + h/2) = \frac{\vec r(t+h) - \vec r(t)}{h}$$

acceleration = change in velocity per unit time

$$\vec a(t) = \frac{\vec v(t+h/2) - \vec v(t-h/2)}{h} = \frac{\vec f}{m}$$

$\Rightarrow$

$$\left.\begin{aligned} \vec v(t+h/2) &:= \vec v(t-h/2) + \vec a(t)h \\ \vec r(t+h) &:= \vec r(t) + \vec v(t+h/2)h \\ t &:= t+h \end{aligned}\right\} \text{repeated}$$



- equivalent to Verlet (identical trajectory)
  but: velocities at different time, a bit different (by $\mathcal{O}(h^2)$) kinetic energy

Equivalence of Verlet and leap-frog

Leap-frog:

$$\left.\begin{aligned} v(t+h/2) &:= v(t-h/2) + a(t)h \\ r(t+h) &:= r(t) + v(t+h/2)h \\ t &:= t+h \end{aligned}\right\} \text{repeated}$$

2nd equation twice in 2 different times:

$$\begin{aligned} r(t+h) &= r(t) + v(t+h/2)h & \times +1 \\ r(t) &= r(t-h) + v(t-h/2)h & \times -1 \end{aligned}$$

Subtract both equations:

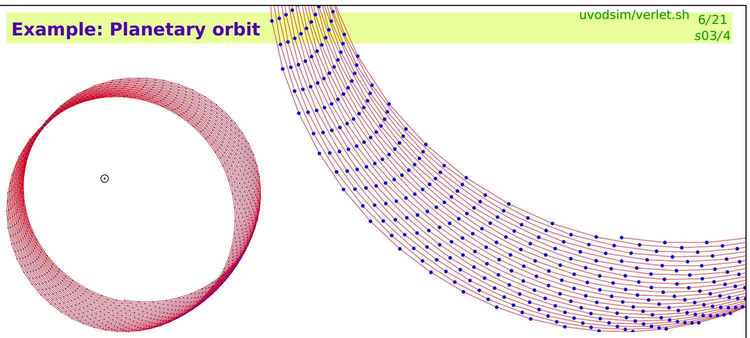
$$r(t+h) - r(t) = r(t) - r(t-h) + v(t+h/2)h - v(t-h/2)h$$

insert for the difference of velocities:

$$r(t+h) - 2r(t) + r(t-h) = h[v(t+h/2) - v(t-h/2)] = a(t)h^2 = \frac{f(t)}{m}h^2$$

which is the Verlet method

Example: Planetary orbit



- energy is well conserved
- perihelion precession $\mathcal{O}(h^2)$
- harmonic oscillator: frequency shifted $\mathcal{O}(h^2)$

Theoretical mechanics and environs

Euler–Lagrange equations

Our world: $\vec r^N = \{\vec r_1, \dots, \vec r^N\}$, $\dot{\vec r}^N = \{\dot{\vec r}_1, \dots, \dot{\vec r}^N\}$

Function $\mathcal{L} = \mathcal{L}(\vec r^N, \dot{\vec r}^N)$

Action:

$$S = \int_{t_0}^{t_1} \mathcal{L}\,\mathrm{d}t$$

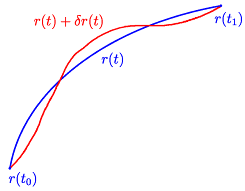
is stationary (likely min or max) between fixed points $\vec r^N(t_0)$ and $\vec r^N(t_1)$ for

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial \mathcal{L}}{\partial \dot{\vec r}_i} = \frac{\partial \mathcal{L}}{\partial \vec r_i}$$

Total $3N$ equations.
If $\mathcal{L}$ = Lagrangian, then this is the **Hamilton principle**, or (in general) the “principle of minimum action” or so.

Euler–Lagrange equations – proof

$$S = \int_{t_0}^{t_1} \mathcal{L}\,\mathrm{d}t$$



Trajectory **variation**:

$$\vec r^N(t) \to \vec r^N(t) + \delta\vec r^N(t), \quad \delta\vec r^N(t_0) = \delta\vec r^N(t_1) = 0$$

$$\delta S = \int_{t_0}^{t_1} \sum_i \frac{\partial \mathcal{L}}{\partial \vec r_i}\cdot\delta\vec r_i\,\mathrm{d}t + \int_{t_0}^{t_1} \sum_i \frac{\partial \mathcal{L}}{\partial \dot{\vec r}_i}\cdot\delta\dot{\vec r}_i\,\mathrm{d}t$$

The 2nd term integrated *by parts*:

$$\delta S = \left[\sum_i \frac{\partial \mathcal{L}}{\partial \dot{\vec r}_i}\cdot\delta\vec r_i\right]_{t_0}^{t_1} + \int_{t_0}^{t_1} \sum_i \delta\vec r_i \cdot \left[\frac{\partial \mathcal{L}}{\partial \vec r_i} - \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial \mathcal{L}}{\partial \dot{\vec r}_i}\right]\mathrm{d}t$$

(1st [] = 0 because the endpoints are fixed)
$\delta\vec r_i$ are arbitrary $\Rightarrow$ 2nd [] = 0

Math refreshment: Legendre transform

Let us have $f(x)$, better a convex one.

$$f^* = f - x\frac{\mathrm{d}f}{\mathrm{d}x} \quad \text{“as function of } p = \frac{\mathrm{d}f}{\mathrm{d}x}\text{”}$$

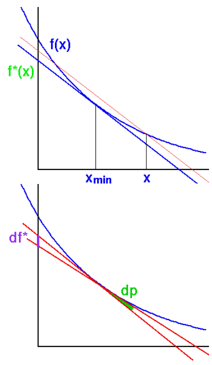
In a more mathematical language:

$$f^*(p) = \min_x (f - xp)$$

Differentials:

$$\mathrm{d}f = \frac{\mathrm{d}f}{\mathrm{d}x}\mathrm{d}x = p\,\mathrm{d}x$$

$$\mathrm{d}f^* = \mathrm{d}f - \mathrm{d}(px) = p\mathrm{d}x - p\mathrm{d}x - x\mathrm{d}p = -x\mathrm{d}p$$



And the reverse transformation:

$$\frac{\mathrm{d}f^*}{\mathrm{d}p} = -x, \quad f^{**} = f^* - \frac{\mathrm{d}f^*}{\mathrm{d}p}p = f^* + px = f$$

A small detour – enthalpy

Internal energy $U = U(S, V)$:

$$\mathrm{d}U = -p\,\mathrm{d}V \quad \text{[ad.]}$$

$U(V)$ [ad.] is convex, because $p = -\frac{\partial U}{\partial V}$ is a decreasing function of V

Enthalpy $H = H(S, p)$:

$$H = U - \frac{\partial U}{\partial V}V = U + pV$$

$$\mathrm{d}H = V\mathrm{d}p \quad \text{[ad.]}$$

Reversed:

$$U = H - Vp = H - \frac{\partial H}{\partial p}p$$

Similarly $U(S) \to F(T)$, $F(N) \to \Omega(\mu)$, …

Example. Plot $F(V)$ and $G(V)$ at constant T for the van der Waals equation of state
control: $a \to T$

From Newton to Lagrange

Let

$$\mathcal{L} = \mathcal{L}(\vec{r}_i^N, \dot{\vec{r}}_i^N) = E_{\rm kin} - E_{\rm pot} = \sum_i \frac{1}{2} m_i \dot{\vec{r}}_i^2 - U(\vec{r}_i^N)$$

then Lagrange equations = Newton's equations

Ummm … nothing new yet.
But in the **generalized coordinates**

$$q_j = q_j(\vec{r}_1, \dots \vec{r}^N), \quad j = 1 \dots 3N$$

it works, too!

Example: planet in the polar coordinates (r, ϕ)

$$\mathcal{L} = E_{\rm kin} - E_{\rm pot} = \frac{1}{2} m(\dot{r}^2 + r^2\dot{\phi}^2) + \frac{K}{r}$$

Euler–Lagrange equations:

$$m\ddot{r} = mr\dot{\phi}^2 - \frac{K}{r^2} \quad \text{(Verlet not applicable)}$$

$$mr^2\ddot{\phi} = 0 \quad \Rightarrow \quad mr^2\dot{\phi} = \text{const} \quad \text{(angular momentum)}$$

From Lagrange to Hamilton

Momentum $\vec{p}_i = m_i \dot{\vec{r}}_i = \frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}_i}$

Generalized momenta (definition): $p_j = \frac{\partial \mathcal{L}}{\partial \dot{q}_j}$

Example (planet): $p_\phi = mr^2\dot{\phi}$

Legendre transform: $\dot{\vec{r}}_i \to \vec{p}_i$ (and opposite sign)

$$\mathcal{H} = \mathcal{H}(\vec{r}^N, \vec{p}^N) = \sum_i \vec{p}_i \cdot \dot{\vec{r}}_i - \mathcal{L}$$

$\mathcal{L} = E_{\rm kin} - E_{\rm pot}$

$\mathcal{H}$ is called the **Hamiltonian**

Cartesian coordinates: $\mathcal{H} = E_{\rm kin} + E_{\rm pot}$

Using the Lagrange equations: $\dot{\vec{p}}_i = \frac{\partial \mathcal{L}}{\partial \vec{r}_i}$

$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}_i} = \frac{\partial \mathcal{L}}{\partial \vec{r}_i}$

⇒ **Hamilton's equations:**

$$\dot{\vec{p}}_i = -\frac{\partial \mathcal{H}}{\partial \vec{r}_i}, \quad \dot{\vec{r}}_i = \frac{\partial \mathcal{H}}{\partial \vec{p}_i}$$

Conservation of energy

Change of $\mathcal{L}$ if both positions and velocities change
(not time: $E_{\rm pot}$ is assumed to be conservative ⇒ $\frac{\partial \mathcal{L}}{\partial t} = 0$)

$$\mathrm{d}\mathcal{L} = \sum_i \left[\frac{\partial \mathcal{L}}{\partial \vec{r}_i} \cdot \mathrm{d}\vec{r}_i + \frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}_i} \cdot \mathrm{d}\dot{\vec{r}}_i\right] = \sum_i (\dot{\vec{p}}_i \cdot \mathrm{d}\vec{r}_i + \vec{p}_i \cdot \mathrm{d}\dot{\vec{r}}_i)$$

Legendre transform:

$$\mathrm{d}\mathcal{H} = \sum_i \mathrm{d}(\vec{p}_i \cdot \dot{\vec{r}}_i) - \mathrm{d}\mathcal{L} = \sum_i [-\dot{\vec{p}}_i \cdot \mathrm{d}\vec{r}_i + \dot{\vec{r}}_i \mathrm{d}\vec{p}_i] \stackrel{!}{=} \sum_i \left[\frac{\partial \mathcal{H}}{\partial \vec{r}_i} \cdot \mathrm{d}\vec{r}_i + \frac{\partial \mathcal{H}}{\partial \vec{p}_i} \cdot \mathrm{d}\vec{p}_i\right]$$

Hamilton equations:

$$\dot{\vec{p}}_i = -\frac{\partial \mathcal{H}}{\partial \vec{r}_i}, \quad \dot{\vec{r}}_i = \frac{\partial \mathcal{H}}{\partial \vec{p}_i}$$

And also:

$$\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} = \sum_i \left[\frac{\partial \mathcal{H}}{\partial \vec{r}_i} \cdot \dot{\vec{r}}_i + \frac{\partial \mathcal{H}}{\partial \vec{p}_i} \cdot \dot{\vec{p}}_i\right] = 0$$

= conservation of energy (Hamiltonian = integral of motion)

A sledgehammer not needed to crack a nut

$$\frac{\mathrm{d}}{\mathrm{d}t}(E_{\rm kin} + E_{\rm pot}) = \frac{\mathrm{d}}{\mathrm{d}t}\left[\sum_i \frac{m_i}{2}\dot{\vec{r}}_i^2 + U(\vec{r}^N)\right]$$

$$= \sum_i \left[m_i \dot{\vec{r}}_i \cdot \ddot{\vec{r}}_i + \frac{\partial U}{\partial \vec{r}_i} \cdot \dot{\vec{r}}_i\right] = \sum_i \dot{\vec{r}}_i \cdot [m_i \ddot{\vec{r}}_i - \vec{f}_i] = 0$$

More integrals of motion: Noether theorem

Any (differentiable) symmetry (of the action) of a physical system has a corresponding conservation law.

- Time → energy conservation
  (assuming $E_{\rm pot}(t) = E_{\rm pot}(t + \delta t)$)
- Translation → momentum

$$U(\vec{r}^N + \delta\vec{r}) = U(\vec{r}^N) \quad \Rightarrow \quad 0 = \delta\vec{r} \cdot \sum_i \frac{\partial U}{\partial \vec{r}_i} = -\delta\vec{r} \cdot \frac{\mathrm{d}}{\mathrm{d}t}\sum_i m_i \dot{\vec{r}}_i$$

  Since $\delta\vec{r}$ is arbitrary, total momentum is conserved

- Rotation → angular momentum

$$U(\vec{r}^N + \delta\vec{\alpha} \times \vec{r}^N) = U(\vec{r}^N)$$

$$\Rightarrow \quad 0 = \sum_i (\delta\vec{\alpha} \times \vec{r}_i) \cdot \frac{\partial U}{\partial \vec{r}_i} = -\sum_i (\delta\vec{\alpha} \times \vec{r}_i) \cdot m_i \ddot{\vec{r}}_i$$

$$= -\sum_i \delta\vec{\alpha} \cdot (\vec{r}_i \times m_i \ddot{\vec{r}}_i) = -\delta\vec{\alpha} \cdot \frac{\mathrm{d}}{\mathrm{d}t}\sum_i \vec{r}_i \times m_i \dot{\vec{r}}_i$$

(Amalie) Emmy Noether

credit: Wikipedia

Total angular momentum is conserved

Poisson and Liouville

Let $f = f(\vec{r}^N, \vec{p}^N)$. Time development: $f(t + \mathrm{d}t) = f(t) + \dot{f}\mathrm{d}t$.

$$\frac{\mathrm{d}f}{\mathrm{d}t} \equiv \dot{f} = \sum_i \left[\dot{\vec{r}}_i \cdot \frac{\partial f}{\partial \vec{r}_i} + \dot{\vec{p}}_i \cdot \frac{\partial f}{\partial \vec{p}_i}\right] = \sum_i \left[\frac{\partial \mathcal{H}}{\partial \vec{p}_i} \cdot \frac{\partial f}{\partial \vec{r}_i} - \frac{\partial \mathcal{H}}{\partial \vec{r}_i} \cdot \frac{\partial f}{\partial \vec{p}_i}\right] \equiv \{f, \mathcal{H}\}$$

$\{,\}$ is called the **Poisson bracket**

It holds $\{A, B\} = -\{B, A\}$

If $f = f(\vec{r}^N, \vec{p}^N)$ is an integral of motion, then $\{f, \mathcal{H}\} = 0$.

If $f = f(\vec{r}^N, \vec{p}^N, t)$ is an integral of motion, then $\{f, \mathcal{H}\} + \frac{\partial f}{\partial t} = 0$

Let us define the **Liouville operator**

$$i\hat{L} = \sum_i \left[\dot{\vec{r}}_i \cdot \frac{\partial}{\partial \vec{r}_i} + \dot{\vec{p}}_i \cdot \frac{\partial}{\partial \vec{p}_i}\right] = \sum_i \left[\frac{\partial \mathcal{H}}{\partial \vec{p}_i} \cdot \frac{\partial}{\partial \vec{r}_i} - \frac{\partial \mathcal{H}}{\partial \vec{r}_i} \cdot \frac{\partial}{\partial \vec{p}_i}\right] \equiv i\hat{L}_r + i\hat{L}_p$$

then (for $\frac{\partial f}{\partial t} = 0$)

$$\dot{f} = \{f, \mathcal{H}\} = i\hat{L}f$$

Canonical quantization (Dirac)

Postulate: $\{,\} \to i\hbar[,]$ signs wrong – see Czech version!

E.g.: $\{p, x\} = -1 \;\Rightarrow\; [\hat{p}, \hat{x}] = -i\hbar$
(x, p = any pair of conjugate canonical variables)

x-representation: $\psi = \psi(x)$, $\hat{x} = x$, $\hat{p} = -i\hbar\frac{\partial}{\partial x}$

In other words $[-i\hbar\frac{\partial}{\partial x}, x]\psi = -i\hbar\psi$ (well-known)

Test of the machinery: $\{p, f\} = -\frac{\partial f}{\partial x} \;\to\; [-i\hbar\frac{\partial}{\partial x}, f]\psi = -i\hbar\frac{\partial}{\partial x}f\psi$

Similarly for $f = f(\vec{r}^N, \vec{p}^N, t)$:

$$\{f, \mathcal{H}\} = \frac{\partial f}{\partial t} \;\to\; [f, \hat{H}] = i\hbar\frac{\partial f}{\partial t} \quad \text{i.e.,} \quad [f, \hat{H}]\psi = i\hbar\frac{\partial}{\partial t}f\psi$$

Satisfied by $\hat{H} = i\hbar\frac{\partial}{\partial t}$ (time Schrödinger equation); we write it as

$$\hat{H}\psi = i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\psi$$

= time development of $\psi(x)$ (x cannot depend on time)

Liouville

$$\dot{f} = i\hat{L}f$$

Formal (operator) solution (separation of variables)

$$\ln f = i\hat{L}t, \quad f(t) = \exp(i\hat{L}t) = \lim_{n\to\infty}(1 + i\hat{L}t/n)^n$$

What does this mean?

- consecutively $n\times$ repeated (approximately)

$$f(0 + t/n) = (1 + i\hat{L}t/n)f(0) = f(0) + \frac{\mathrm{d}f}{\mathrm{d}t}_{|t=0} t/n$$

- Taylor:

$$\exp(i\hat{L}t)f(0) = 1 + (i\hat{L}f)t + (i\hat{L}i\hat{L}f)\frac{t^2}{2} + \dots =$$

$$= 1 + \dot{f}(0)t + \ddot{f}\frac{t^2}{2} + \dots = f(t)$$

Both parts separately

The same Taylor-like trick for $i\hat{L}_r$ and $i\hat{L}_p$:

$$\exp(i\hat{L}_r t)f(\vec{r}^N, \vec{p}^N) = 1 + (i\hat{L}_r f)t + (i\hat{L}_r i\hat{L}_r f)\frac{t^2}{2} + \dots =$$

$$= 1 + \sum_i \dot{\vec{r}}_i \cdot \frac{\partial f}{\partial \vec{r}_i} t + \sum_j \dot{\vec{r}}_j \sum_i \dot{\vec{r}}_i : \frac{\partial^2 f}{\partial \vec{r}_i \vec{r}_j}\frac{t^2}{2} + \dots = f(\vec{r}^N + \dot{\vec{r}}^N t, \vec{p}^N)$$

$$\exp(i\hat{L}_p t)f(\vec{r}^N, \vec{p}^N) = f(\vec{r}^N, \vec{p}^N + \dot{\vec{p}}^N t)$$

Problem: operators $i\hat{L}_p$ and $i\hat{L}_r$ do not commute:

$$\exp(i\hat{L}) = \exp(i\hat{L}_p + i\hat{L}_r) \neq \exp(i\hat{L}_p)\exp(i\hat{L}_r)$$

Verlet once again

So let at least approximately (for small h), but always reversibly:

$$\exp(i\hat{L}h) \approx \exp(i\hat{L}_p h/2)\exp(i\hat{L}_r h)\exp(i\hat{L}_p h/2)$$

Step by step (^{N} omitted):

$$\begin{array}{lccl}
(& \vec{p}(0) & , & \vec{r}(0) &) \\
(& \vec{p}(0) + \dot{\vec{p}}(0)h/2 & , & \vec{r}(0) &) \\
(& \vec{p}(0) + \dot{\vec{p}}(0)h/2 & , & \vec{r}(0) + (1/m)[\vec{p}(0) + \dot{\vec{p}}(0)h/2]h &) \\
(& \vec{p}(0) + [\dot{\vec{p}}(0) + \dot{\vec{p}}(h)]h/2 & , & \vec{r}(0) + (1/m)[\vec{p}(0) + \dot{\vec{p}}(0)h/2]h &)
\end{array}$$

This is the so called **velocity Verlet**:

$$r(t + h) = r(t) + v(t)h + \frac{f(t)}{m}\frac{h^2}{2}$$

$$v(t + h) = v(t) + \frac{f(t) + f(t + h)}{m}\frac{h}{2}$$

The same trajectory as Verlet with $v(t) = \frac{r(t + h) - r(t - h)}{2h}$

What is this good for?

$$\exp(i\hat{L}_p h/2)\exp(i\hat{L}_r h)\exp(i\hat{L}_p h/2) = \exp(i\hat{L}h + \epsilon)$$

- error ϵ can be estimated ($\propto h^3$)
- we can calculate a "perturbed Hamiltonian" (error $\mathcal{O}(h^3)$ per step, $\mathcal{O}(h^2)$ globally), exactly constant with the Verlet method
  i.e., Verlet is **symplectic** $\Rightarrow$ error is bound
  (time reversibility $\Rightarrow$ only error $\propto t^{1/2}$)

The error of energy conservation is use to set the timestep h, more in the following talk.

- multiple-timestep methods and higher-order methods