L5 - Classical Mechanics 1

Newton’s Laws

A quick math remainder

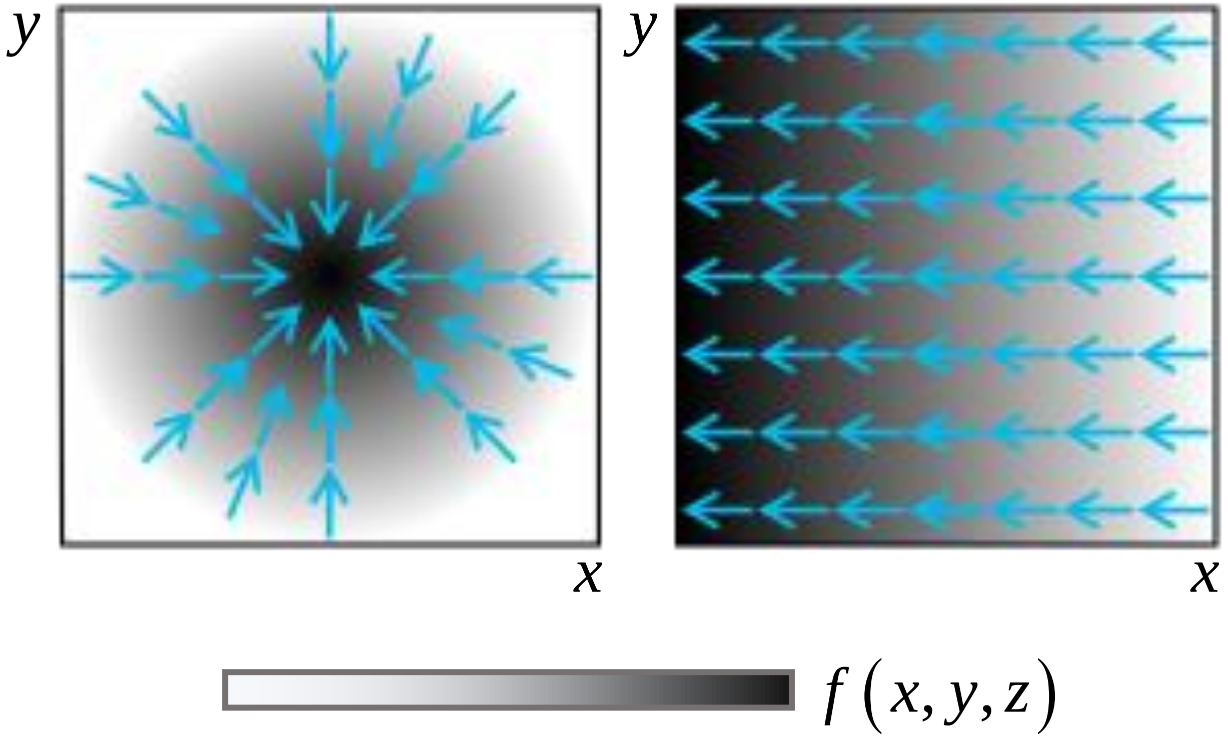
The gradient of a function

Suppose we have a scalar function

$$f(x, y, z)$$

The gradient of f is the vector

$$\nabla f(x, y, z) = \left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z} \right) = \vec{\mathbf{g}}(x, y, z)$$



Example: Consider the function

$$f\left(x,y,z\right)=-\sqrt{x^2+y^2+z^2}$$

The gradient is

$$\nabla f=\left(-\frac{x}{\sqrt{x^2+y^2+z^2}},-\frac{y}{\sqrt{x^2+y^2+z^2}},-\frac{z}{\sqrt{x^2+y^2+z^2}}\right)$$

The cross product of two vectors

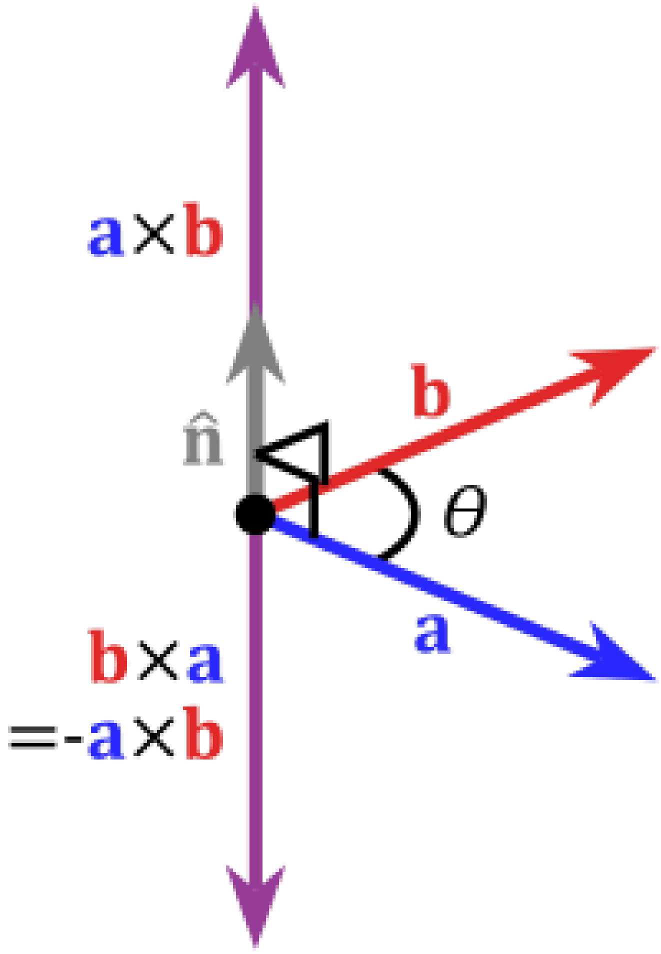
Suppose we have two vectors **a** and **b**

If their norms are

$$\|\mathbf{a}\| = \sqrt{a_x^2 + a_y^2 + a_z^2} \qquad \|\mathbf{b}\| = \sqrt{b_x^2 + b_y^2 + b_z^2}$$

Their cross product is

$$\mathbf{a} \times \mathbf{b} = \|\mathbf{a}\| \|\mathbf{b}\| \sin(\theta) \hat{\mathbf{n}}$$



Mechanics of a particle

Consider a single particle with mass *m* and position **r**.

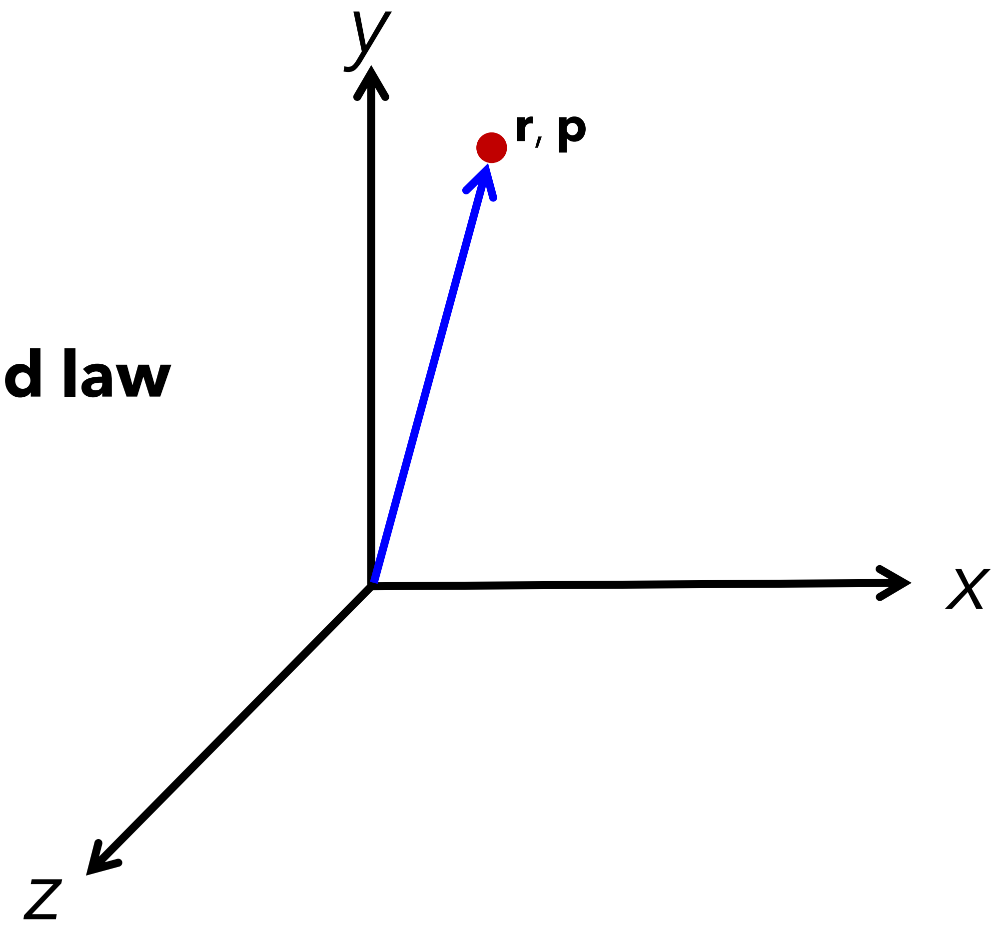
The velocity is $\mathbf{v} \equiv \frac{d\mathbf{r}}{dt}$

The linear momentum is $\mathbf{p} \equiv m\mathbf{v}$

The motion is determined by **Newton's second law**

$$\frac{d\mathbf{p}}{dt} = \mathbf{F}$$

F is a force acting on the particle.



The acceleration is defined as:

$$\mathbf{a} \equiv \frac{d^2\mathbf{r}}{dt^2}$$

If the mass is constant, Newton's second law becomes $\mathbf{F} = m\mathbf{a}$

$$\frac{d\mathbf{p}}{dt} = \mathbf{F}$$

$$\frac{d\mathbf{p}}{dt} = \frac{d(m\mathbf{v})}{dt} = m\frac{d\mathbf{v}}{dt} = m\frac{d}{dt}\left(\frac{d\mathbf{r}}{dt}\right) = m\frac{d^2\mathbf{r}}{dt^2} = m\mathbf{a}$$

$$m\mathbf{a} = \mathbf{F}$$

Newton’s second law

$$\frac{d^2\mathbf{r}}{dt^2} = \frac{\mathbf{F}}{m}$$

Newton’s second law is valid in an inertial or Galilean system.

Conservation of linear momentum of a particle

If the total force **F** is zero, then the linear momentum **p** is conserved

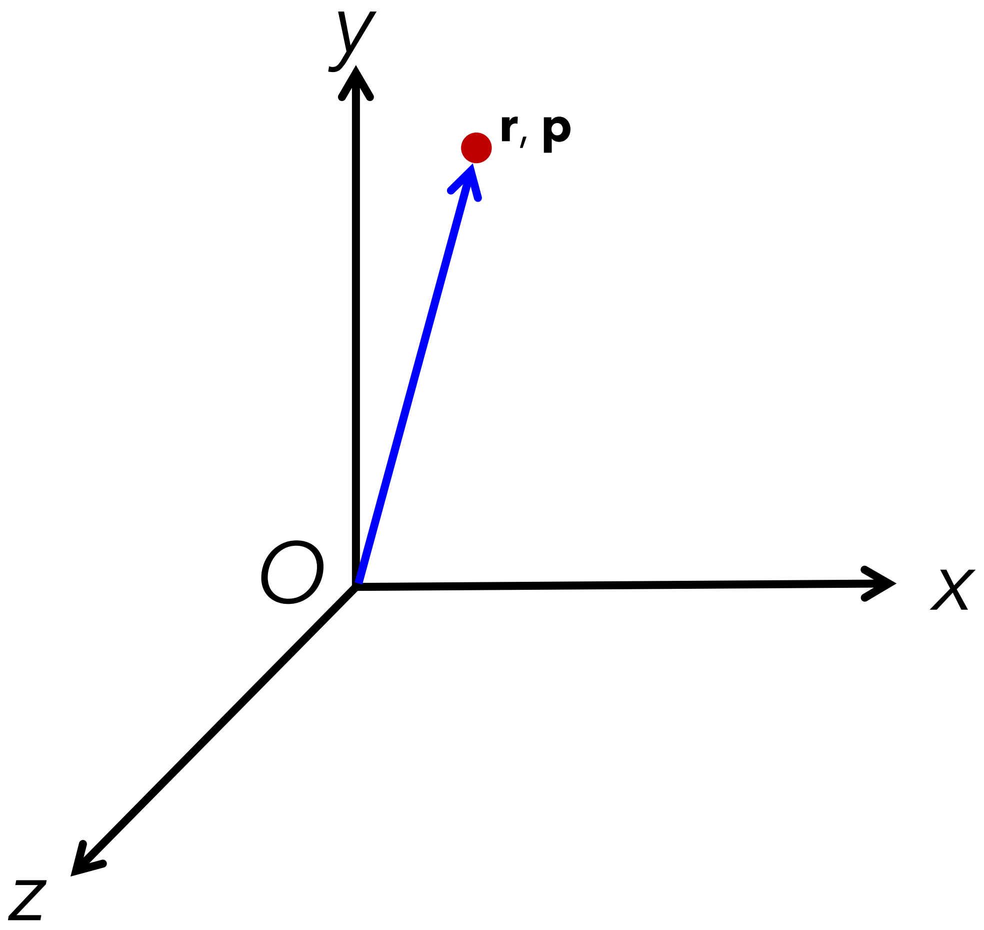
$$\frac{d\mathbf{p}}{dt} = 0 \rightarrow \mathbf{p} \text{ is a constant } \textbf{(Newton's first law)}$$

The angular momentum about O is

$$\mathbf{L} \equiv \mathbf{r} \times \mathbf{p}$$

The torque about O is

$$\mathbf{N} \equiv \mathbf{r} \times \mathbf{F}$$



To get the angular equation of motion

$$\frac{d(m\mathbf{v})}{dt} = \mathbf{F}$$

$$\mathbf{r} \times \frac{d(m\mathbf{v})}{dt} = \mathbf{r} \times \mathbf{F}$$

$$\frac{d(\mathbf{r} \times m\mathbf{v})}{dt} = \underbrace{\mathbf{v} \times m\mathbf{v}}_{0} + \mathbf{r} \times \frac{d(m\mathbf{v})}{dt} = \mathbf{r} \times \frac{d(m\mathbf{v})}{dt}$$

$$\frac{d(\mathbf{r} \times m\mathbf{v})}{dt} = \mathbf{r} \times \mathbf{F}$$

$$\boxed{\frac{d\mathbf{L}}{dt} = \mathbf{N}}$$

Conservation of angular momentum of a particle

If the total torque **N** is zero, then the angular momentum **L** is conserved

$$\frac{d\mathbf{L}}{dt} = 0 \rightarrow \mathbf{L} \text{ is a constant}$$

The work done to move the particle from 1 to 2 along **s** is

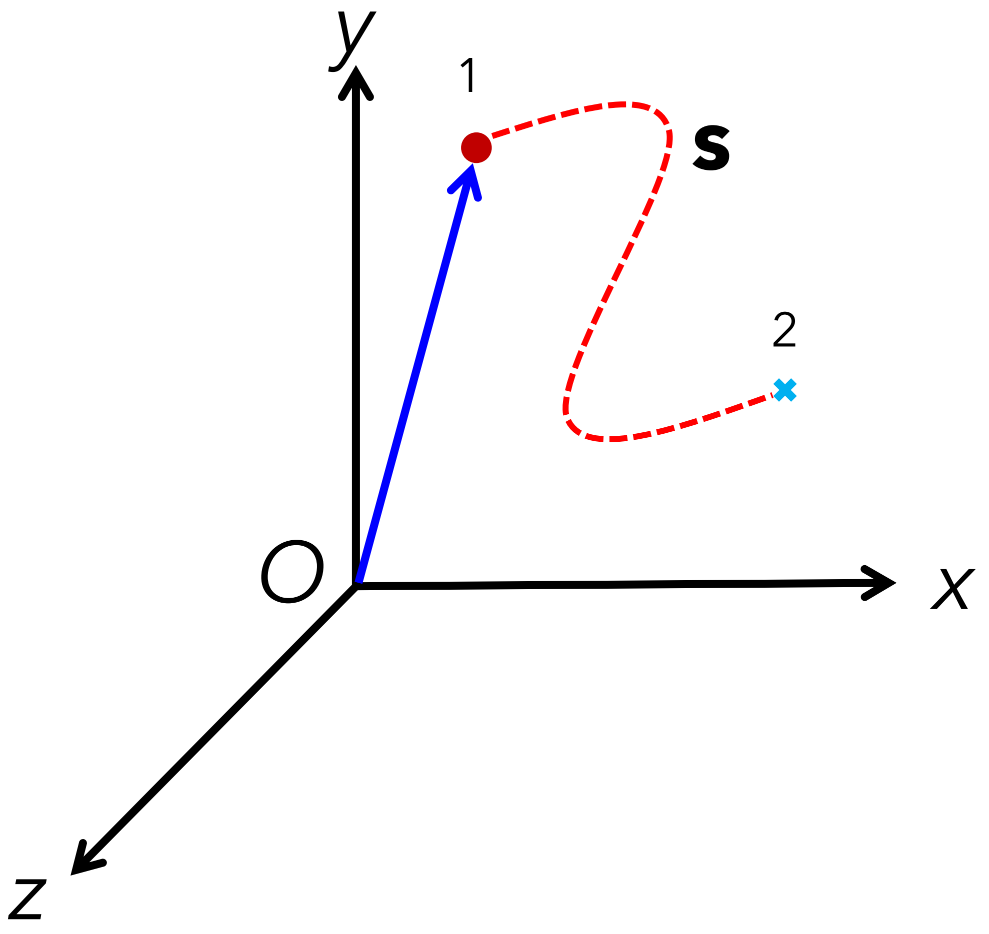
$$W_{12} \equiv \int_1^2 \mathbf{F} \cdot d\mathbf{s}$$

If the mass is constant

$$W_{12} = \int_1^2 \mathbf{F} \cdot d\mathbf{s} = m\int_1^2 \frac{d\mathbf{v}}{dt} \cdot \mathbf{v}dt$$

$$\frac{d\mathbf{v}}{dt} \cdot \mathbf{v} = \frac{1}{2}\frac{d}{dt}\mathbf{v}^2$$

$$W_{12} = \frac{1}{2}m\int_1^2 \left(\frac{d}{dt}\mathbf{v}^2\right)dt = \frac{1}{2}m\left(\mathbf{v}_2^2 - \mathbf{v}_1^2\right)$$

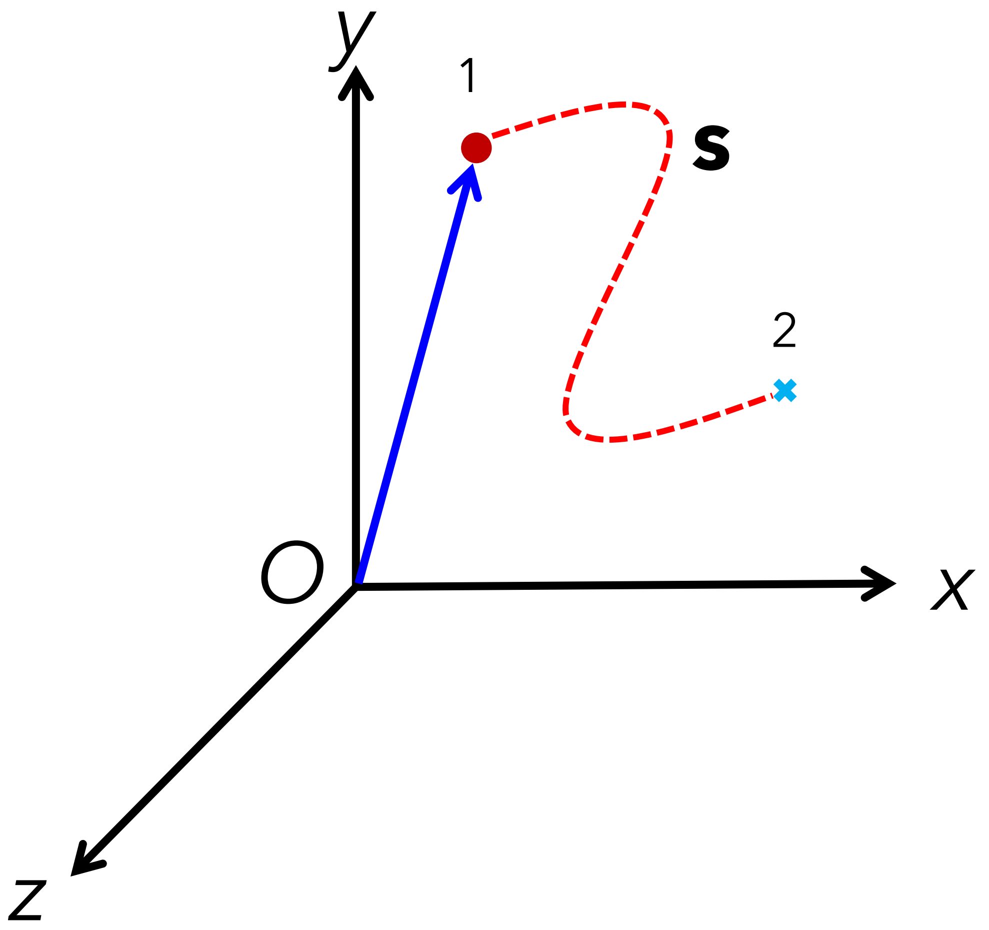


The kinetic energy is defined as

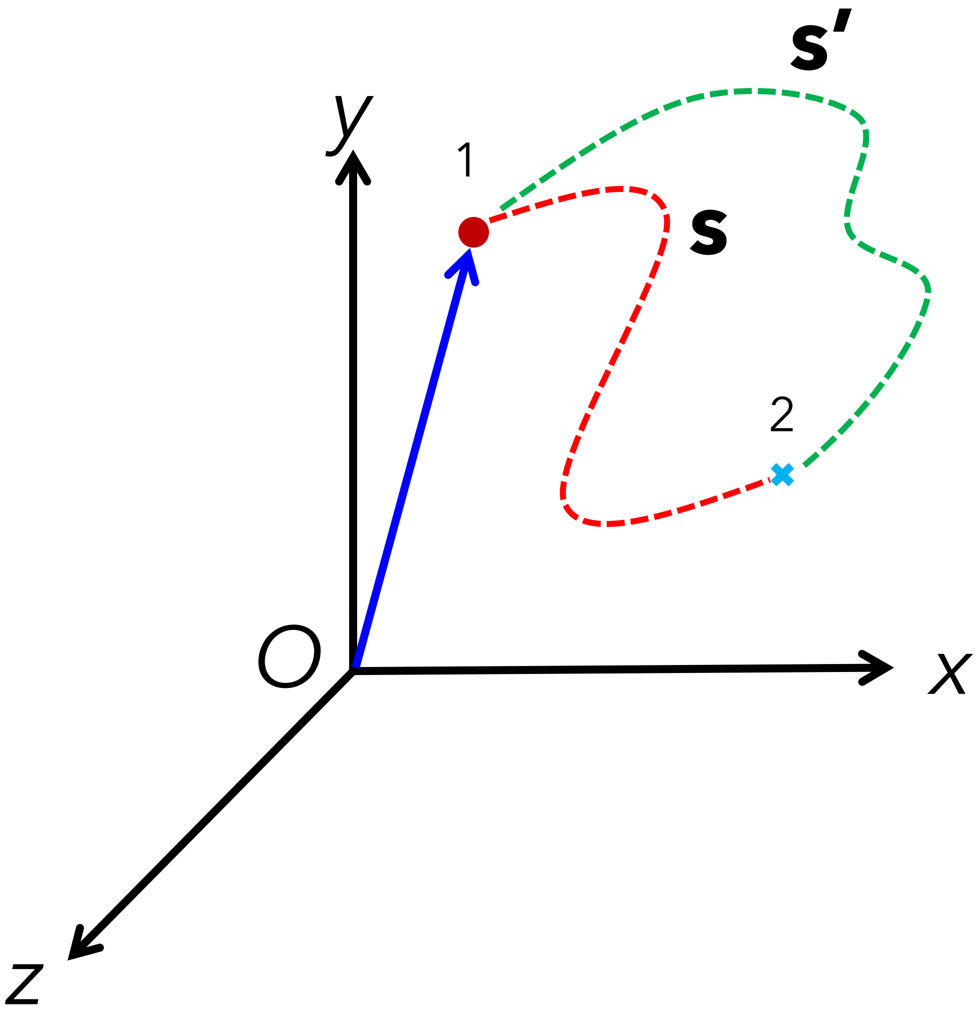
$$T \equiv \frac{1}{2} m \mathbf{v}^2$$

The work is the variation of kinetic energy

$$W_{12} = \frac{1}{2} m \left(\mathbf{v}_2^2 - \mathbf{v}_1^2 \right)$$
$$= T_2 - T_1$$

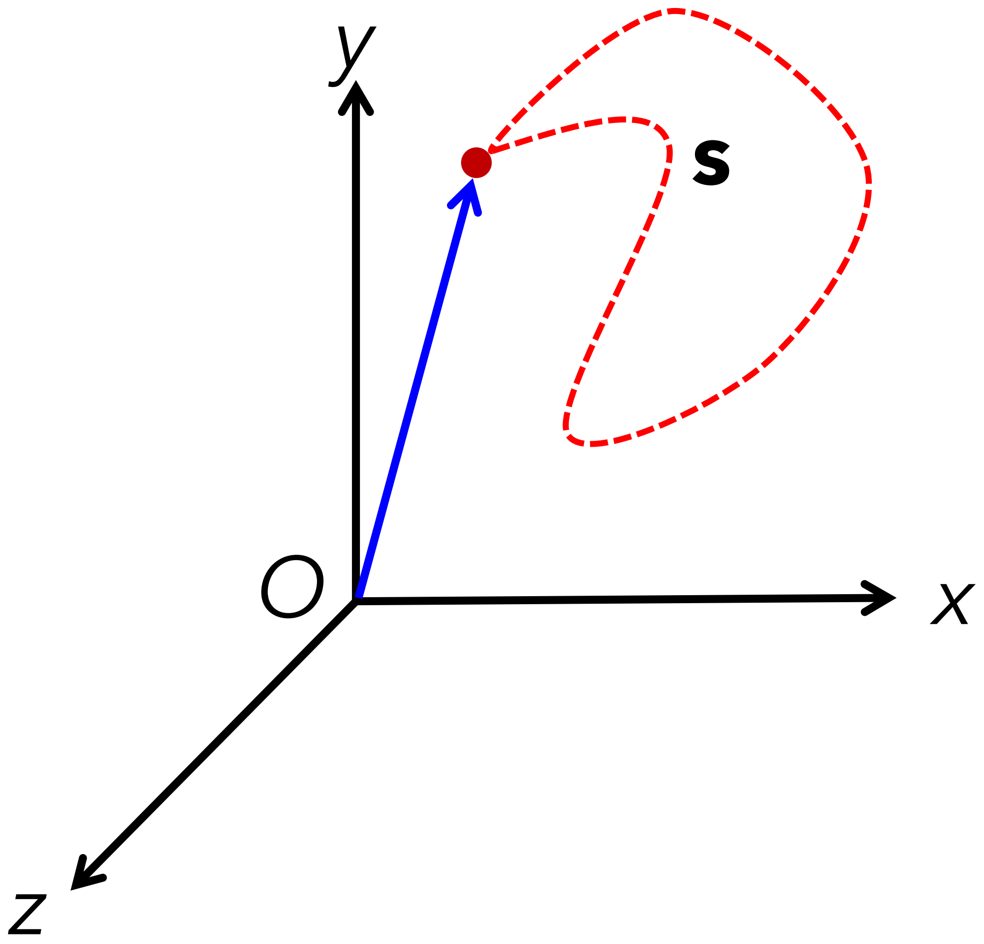


If **F** is such that W_{12} is always the same no matter **s**,
F is called **conservative**.



F is conservative if

$$\oint \mathbf{F} \cdot d\mathbf{s} = 0$$



If **F** is conservative, it can be written as the negative of the gradient of a scalar potential *V* that depends only on **r**.

$$\mathbf{F} = -\nabla V(\mathbf{r})$$

The work in terms of the potential is

$$W_{12} = \int_1^2 \mathbf{F} \cdot d\mathbf{s} = -\int_1^2 \nabla V(\mathbf{r}) \cdot d\mathbf{s} = V_1 - V_2$$

We have

$$W_{12} = V_1 - V_2 = T_2 - T_1$$

Thus

$$T_1 + V_1 = T_2 + V_2$$

Energy conservation for a particle

If **F** is conservative, then the $E = T + V$ is constant.

Mechanics of a system of particles

Consider a system of **2 isolated particles**

The total momentum is $\mathbf{p} = \mathbf{p}_1 + \mathbf{p}_2$

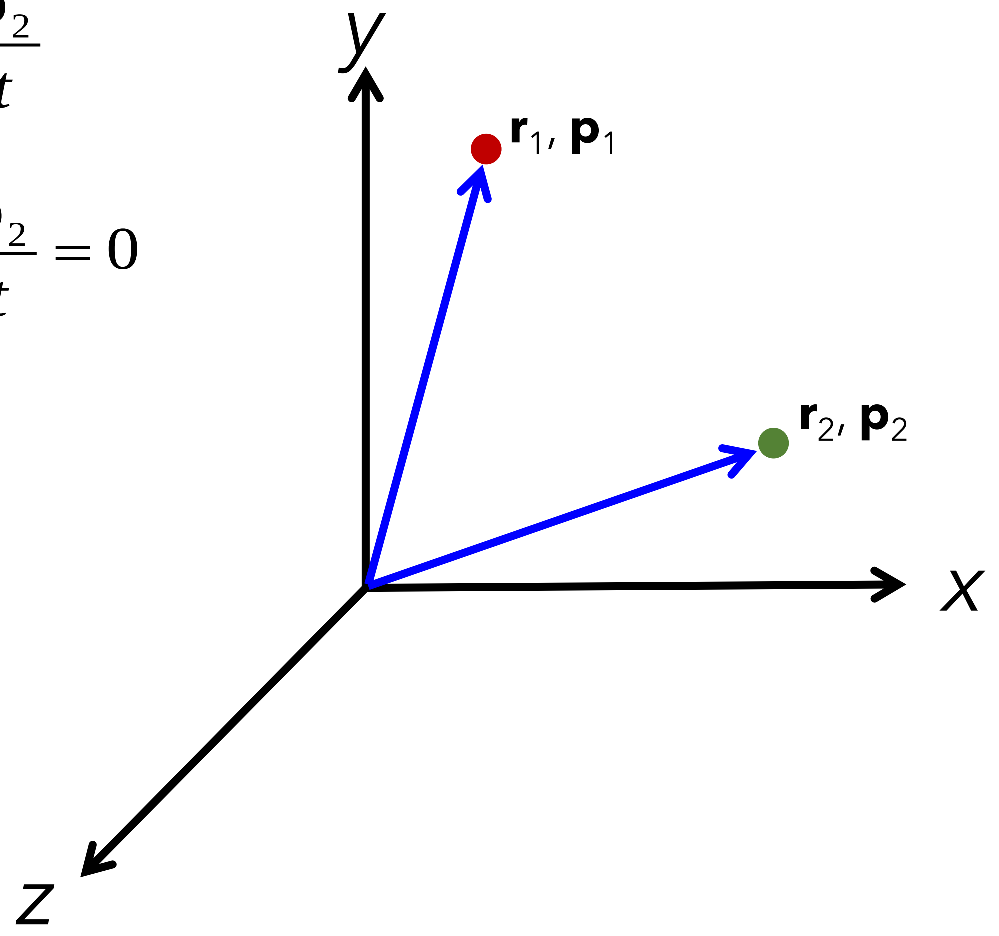
The total momentum variation is $\frac{d\mathbf{p}}{dt} = \frac{d\mathbf{p}_1}{dt} + \frac{d\mathbf{p}_2}{dt}$

If the two particles are isolated: $\frac{d\mathbf{p}}{dt} = \frac{d\mathbf{p}_1}{dt} + \frac{d\mathbf{p}_2}{dt} = 0$

Therefore, $\frac{d\mathbf{p}_1}{dt} = -\frac{d\mathbf{p}_2}{dt}$

For each body, $\frac{d\mathbf{p}_1}{dt} = \mathbf{F}_{21}$ *and* $\frac{d\mathbf{p}_2}{dt} = \mathbf{F}_{12}$

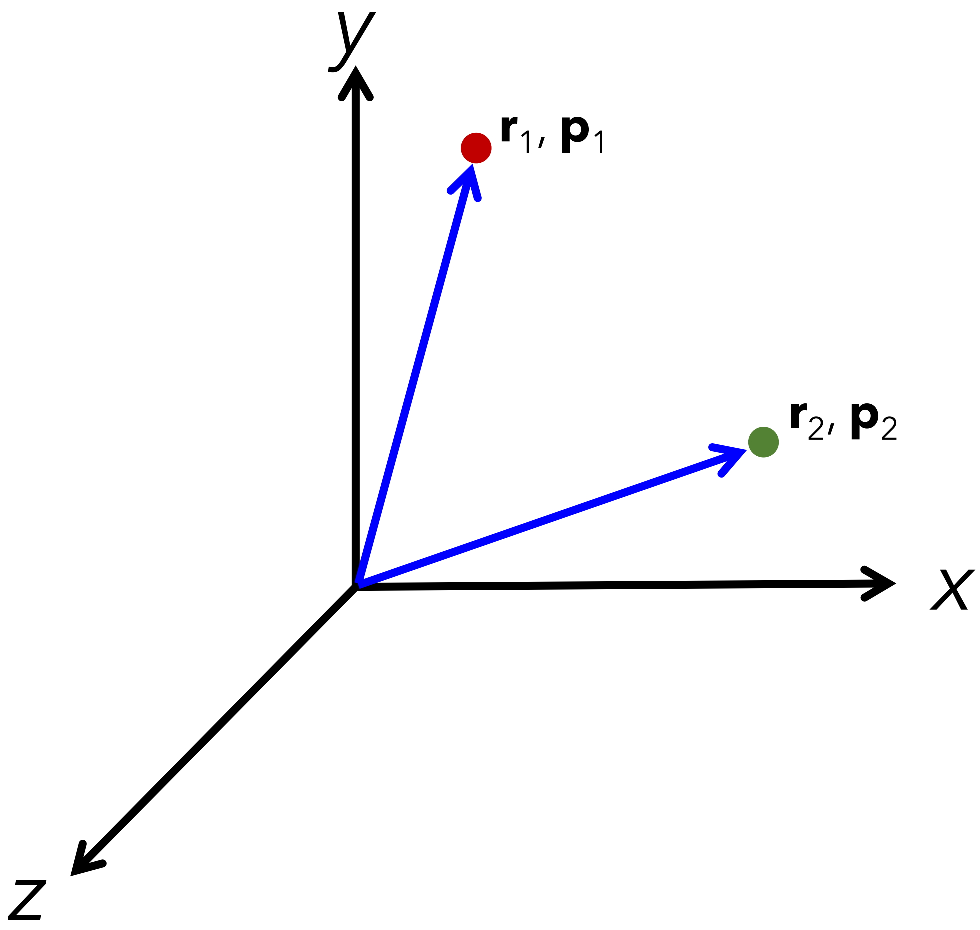
Thus, $\mathbf{F}_{21} = -\mathbf{F}_{12}$ **(Newton's third law)**



Consider a system of ***N* particles**

Newton's second law determines the motion of particle *i*

$$\frac{d\mathbf{p}_i}{dt} = \sum_{j=1(\neq i)}^{N} \left[\mathbf{F}_{ji} + \mathbf{F}_i^{(e)} \right]$$



$\mathbf{F}_{ji}$ is the force on i due to j

$\mathbf{F}_i^{(e)}$ is an external force

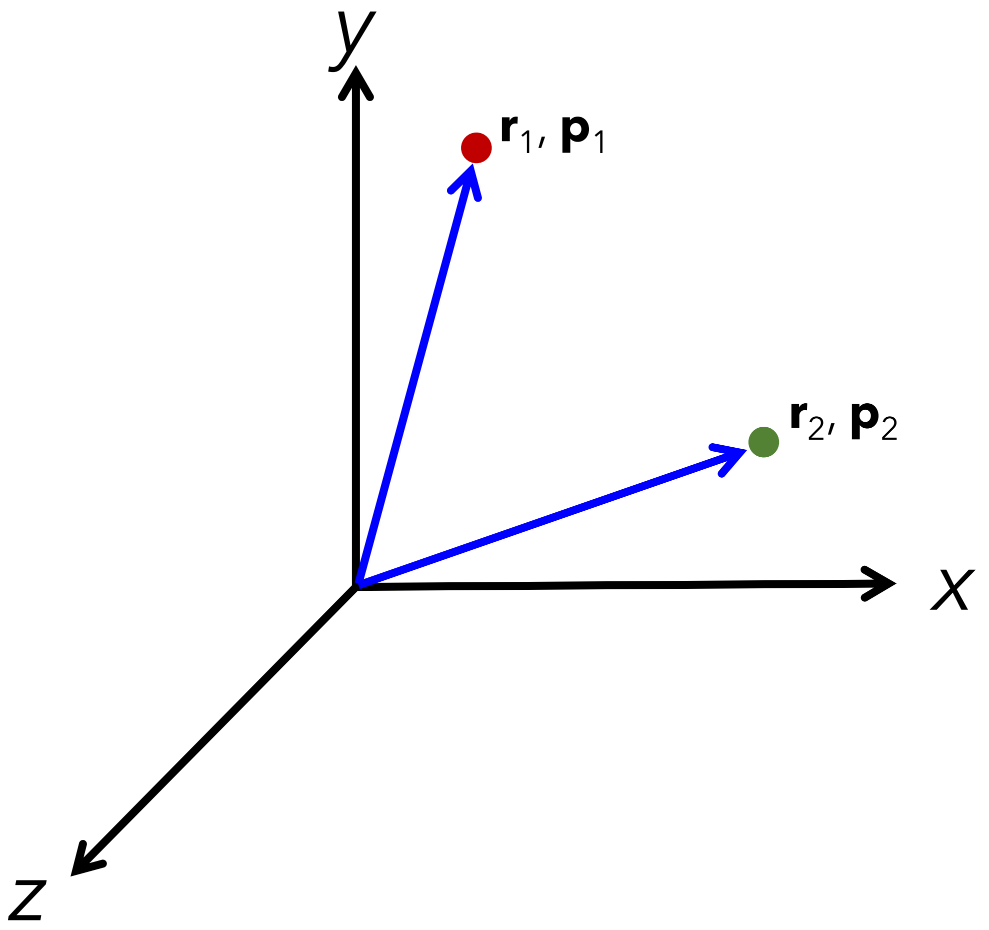
The center of mass

Sum over all particles

$$\sum_{i=1}^{N} m_i \frac{d^2\mathbf{r}_i}{dt^2} = \sum_{i=1}^{N}\left[\sum_{j=1(\neq i)}^{N}\left[\mathbf{F}_{ji} + \mathbf{F}_i^{(e)}\right]\right]$$

Because $\mathbf{F}_{ji} = -\mathbf{F}_{ij}$

$$\sum_{i=1}^{N} m_i \frac{d^2\mathbf{r}_i}{dt^2} = \sum_{i=1}^{N}\mathbf{F}_i^{(e)} = \mathbf{F}^{(e)}$$



$$\sum_{i=1}^{N} m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}^{(e)}$$

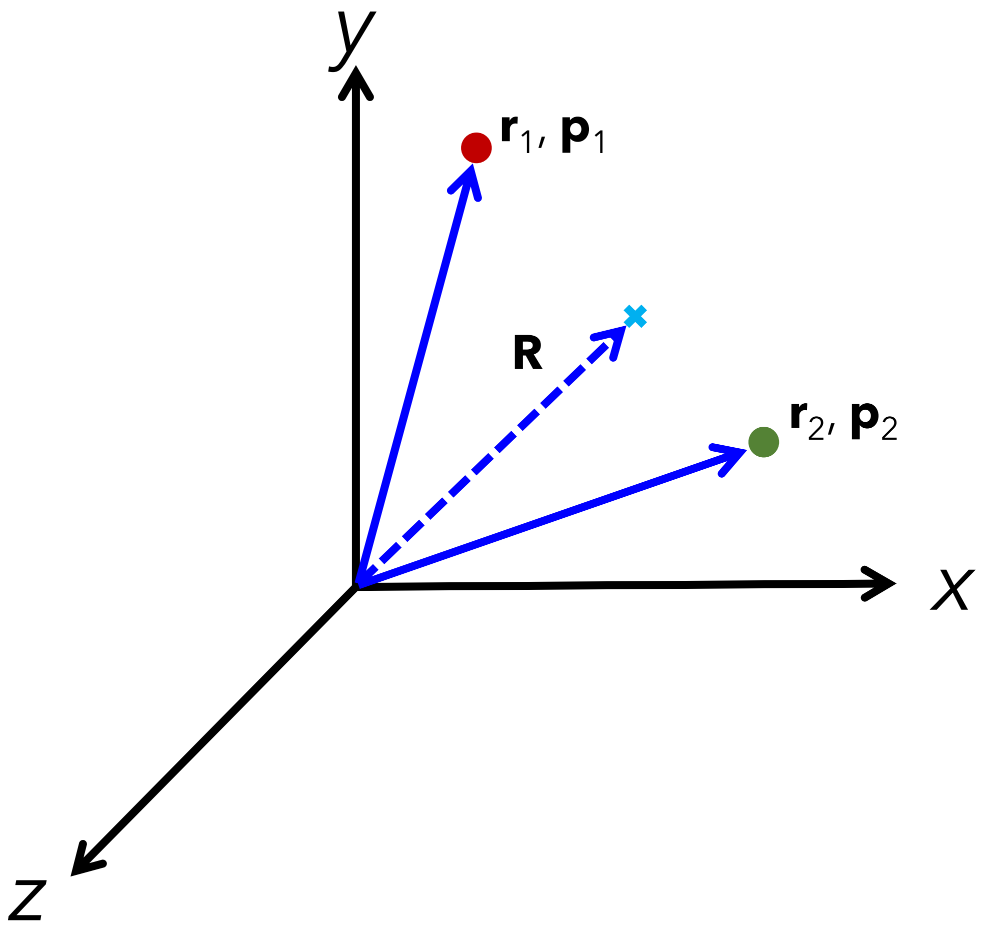
$$\sum_{i=1}^{N} m_i \frac{d^2\mathbf{r}_i}{dt^2} = \frac{d^2}{dt^2}\sum_{i=1}^{N} m_i\mathbf{r}_i$$

$$= M\frac{d^2}{dt^2}\left(\frac{1}{M}\sum_{i=1}^{N} m_i\mathbf{r}_i\right) \qquad M \equiv \sum_{i=1}^{N} m_i$$

$$= M\frac{d^2\mathbf{R}}{dt^2}$$

Position of the center of mass

$$\mathbf{R} \equiv \frac{1}{M}\sum_{i=1}^{N} m_i\mathbf{r}_i$$



Using:

$$\sum_{i=1}^{N} m_i \frac{d^2\mathbf{r}_i}{dt^2} = \sum_{i=1}^{N} \mathbf{F}_i^{(e)} = \mathbf{F}_i^{(e)} \quad and \quad \sum_{i=1}^{N} m_i \frac{d^2\mathbf{r}_i}{dt^2} = M \frac{d^2\mathbf{R}}{dt^2}$$

We get Newton's second law for the sum over all particles

$$M \frac{d^2\mathbf{R}}{dt^2} = \mathbf{F}^{(e)}$$

"The center of mass moves as if the total external force were acting on the entire mass of the system concentrated at the center of mass."

Goldstein, Classical mechanics. **1980**

Conservation of linear momentum of a system of particles

Momentum of the center of mass (total mass is constant)

$$M\frac{d^2\mathbf{R}}{dt^2} = \mathbf{F}^{(e)}$$

$$\frac{d}{dt}\left(M\frac{d\mathbf{R}}{dt}\right) = \frac{d\mathbf{P}}{dt} = \mathbf{F}^{(e)}$$

If the total external force is zero, the total linear momentum is conserved.

$$\frac{d\mathbf{P}}{dt} = 0 \rightarrow \mathbf{P}\text{ is constant}$$

Time-derivative of the total angular momentum

$$\sum_i \frac{d\mathbf{L}_i}{dt} = \sum_i \mathbf{N}_i$$

Left side

$$\sum_i \frac{d\mathbf{L}_i}{dt} = \frac{d}{dt}\sum_i \mathbf{L}_i = \frac{d\mathbf{L}}{dt}$$

Right side

$$\sum_i \mathbf{N}_i = \sum_i \mathbf{r}_i \times \left(\mathbf{F}_i^{(e)} + \sum_{j \neq i} \mathbf{F}_{ji} \right)$$

$$= \sum_i \mathbf{r}_i \times \mathbf{F}_i^{(e)} + \underline{\sum_{\substack{i,j \\ j \neq i}} \mathbf{r}_i \times \mathbf{F}_{ji}}$$

Example with $N = 2$

$$\sum_{\substack{i,j \\ j\neq i}} \mathbf{r}_i \times \mathbf{F}_{ji} = \mathbf{r}_1 \times \mathbf{F}_{21} + \mathbf{r}_2 \times \mathbf{F}_{12}$$

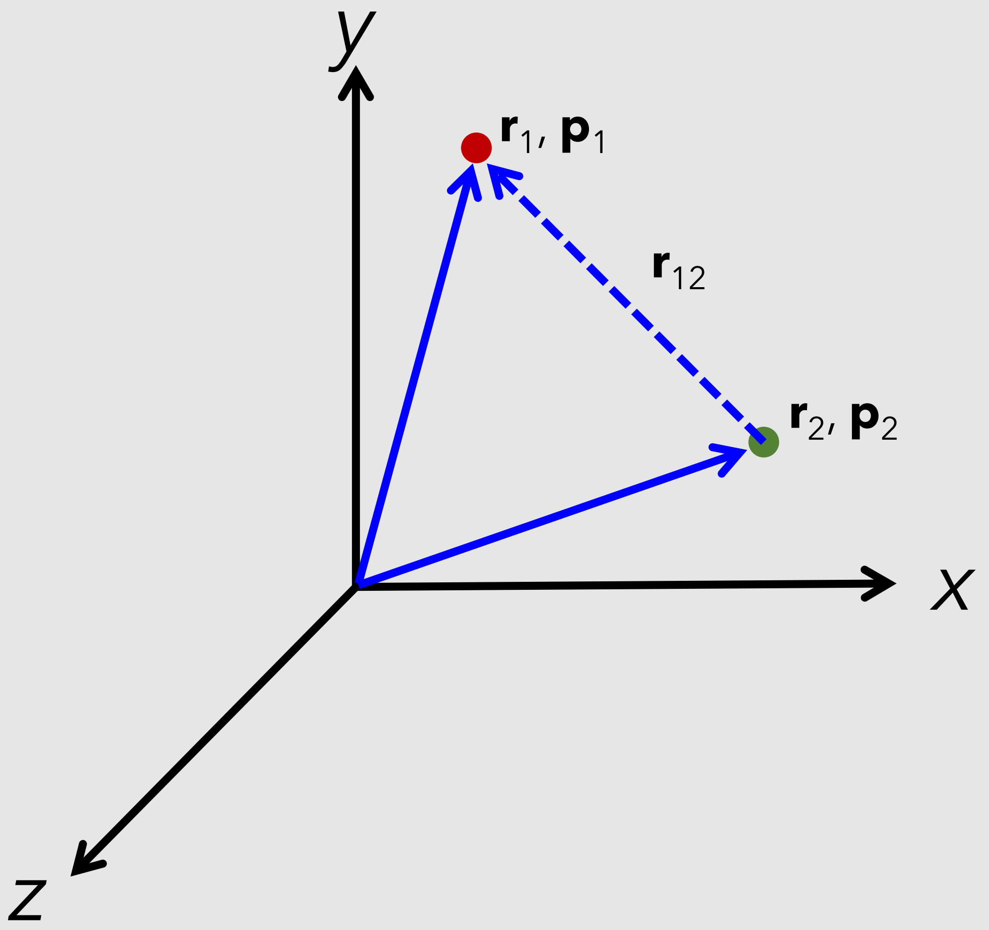
$$= \mathbf{r}_1 \times \mathbf{F}_{21} - \mathbf{r}_2 \times \mathbf{F}_{21}$$

$$= \left(\mathbf{r}_1 - \mathbf{r}_2\right) \times \mathbf{F}_{21}$$

$$= \mathbf{r}_{12} \times \mathbf{F}_{21}$$

For central forces (forces along $\mathbf{r}_{ij}$)

$$\sum_{\substack{i,j \\ j\neq i}} \mathbf{r}_i \times \mathbf{F}_{ji} = 0$$



Time-derivative of the total angular momentum

$$\sum_i \frac{d\mathbf{L}_i}{dt} = \sum_i \mathbf{N}_i$$

Left side

$$\sum_i \frac{d\mathbf{L}_i}{dt} = \frac{d}{dt}\sum_i \mathbf{L}_i = \frac{d\mathbf{L}}{dt}$$

Right side

$$\sum_i \mathbf{N}_i = \sum_i \mathbf{r}_i \times \left(\mathbf{F}_i^{(e)} + \sum_{j \neq i} \mathbf{F}_{ji} \right)$$

$$= \sum_i \mathbf{r}_i \times \mathbf{F}_i^{(e)} + \underline{\sum_{\substack{i,j \\ j \neq i}} \mathbf{r}_i \times \mathbf{F}_{ji}} = \sum_i \mathbf{r}_i \times \mathbf{F}_i^{(e)} = \mathbf{N}^{(e)} \text{ (for central forces)}$$

= 0 (for central forces)

Conservation of angular momentum of a system of particles under central forces

For central forces, the total angular momentum is related to the total external torque through

$$\frac{d\mathbf{L}}{dt} = \mathbf{N}^{(e)}$$

Therefore, if the total external torque is zero, the total angular momentum is conserved.

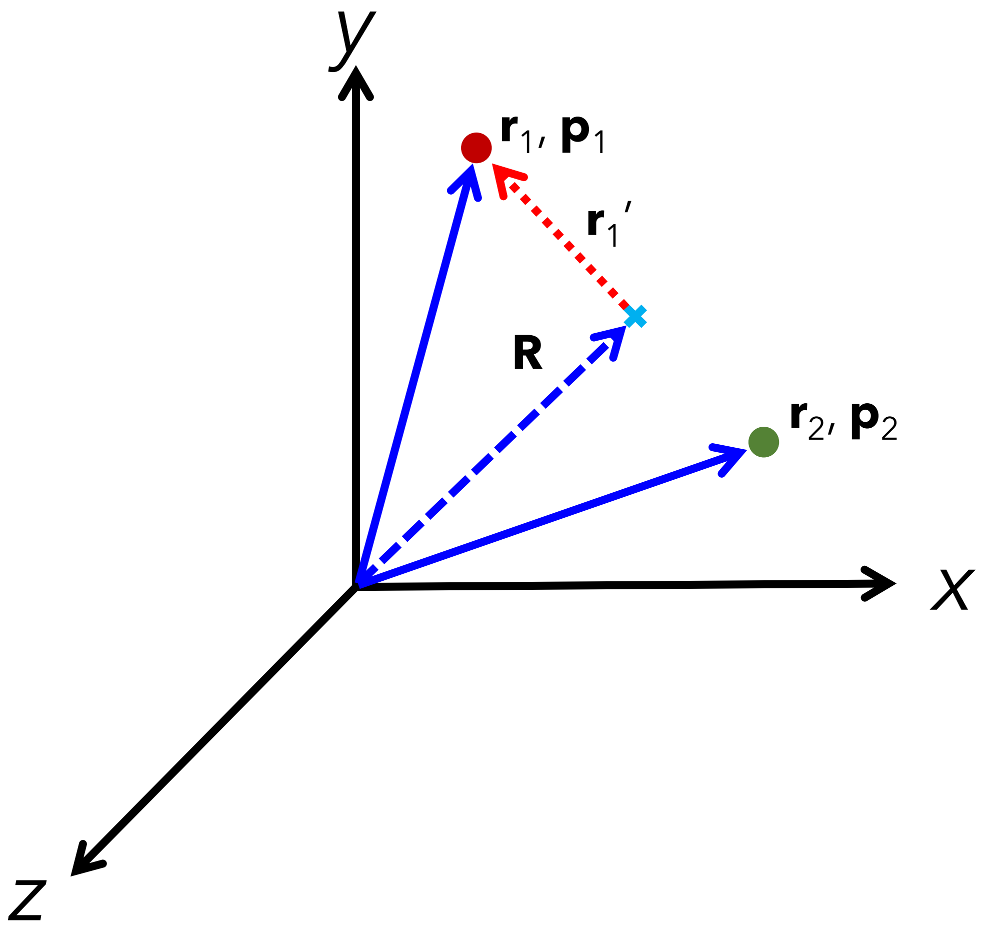
$$\frac{d\mathbf{L}}{dt} = 0 \rightarrow \mathbf{L} \text{ is constant}$$

Lab (absolute) reference and center of mass reference:

$$\mathbf{r}_i = \mathbf{r}_i' + \mathbf{R}$$

$$\frac{d\mathbf{r}_i}{dt} = \frac{d\mathbf{r}_i'}{dt} + \frac{d\mathbf{R}}{dt}$$

$$\mathbf{v}_i = \mathbf{v}_i' + \mathbf{v}$$



We can show that

$$\mathbf{L} = \sum_i \mathbf{r}_i' \times \mathbf{p}_i' + \mathbf{R} \times \mathbf{P}$$

See the demonstration in the appendix to the presentation

The angular momentum about point O is the angular momentum of the center of the mass plus the angular momentum of the motion about the center of mass.

If the center of mass is at rest, the total angular momentum does not depend on a reference point.

The total kinetic energy is the kinetic energy of the center of mass plus the kinetic energy about the center of mass.

$$T = \frac{1}{2} M\mathbf{v}^2 + \frac{1}{2}\sum_i m_i \mathbf{v}_i'^2$$

See the demonstration in the appendix to the presentation

The **work** of a system of particles is the variation of their **potential energy**

$$W_{12} = V_A - V_B$$

See the demonstration in the appendix to the presentation

But only if

1) the external forces are conservative

$$\mathbf{F}_i^{(e)} = -\nabla_i V_i$$

2) the internal forces are conservative and central

$$\mathbf{F}_{ji} = -\nabla V_{ij}\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right)$$

The **work** of a system of particles is the variation of their **kinetic energy**

$$W_{12} = T_B - T_A$$

See the demonstration in the appendix to the presentation

Putting everything together

$$W_{12} = V_A - V_B = T_B - T_A$$

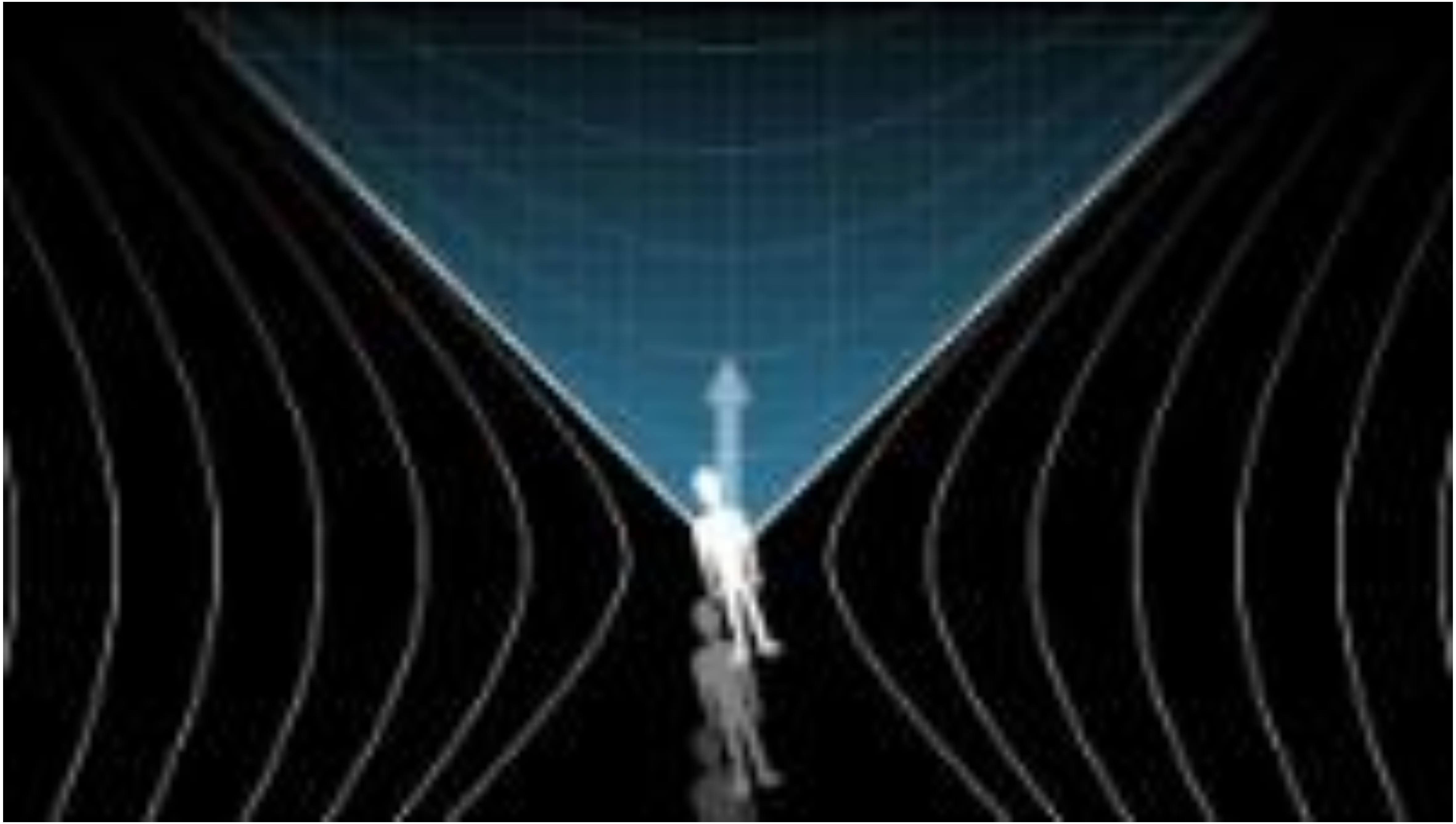
Thus

$$T_A + V_A = T_B + V_B$$

Energy conservation for a system of particles

If the external force is conservative and the internal forces are conservative and central, then $E = T + V$ is constant.

Reference frames
(toward special relativity)



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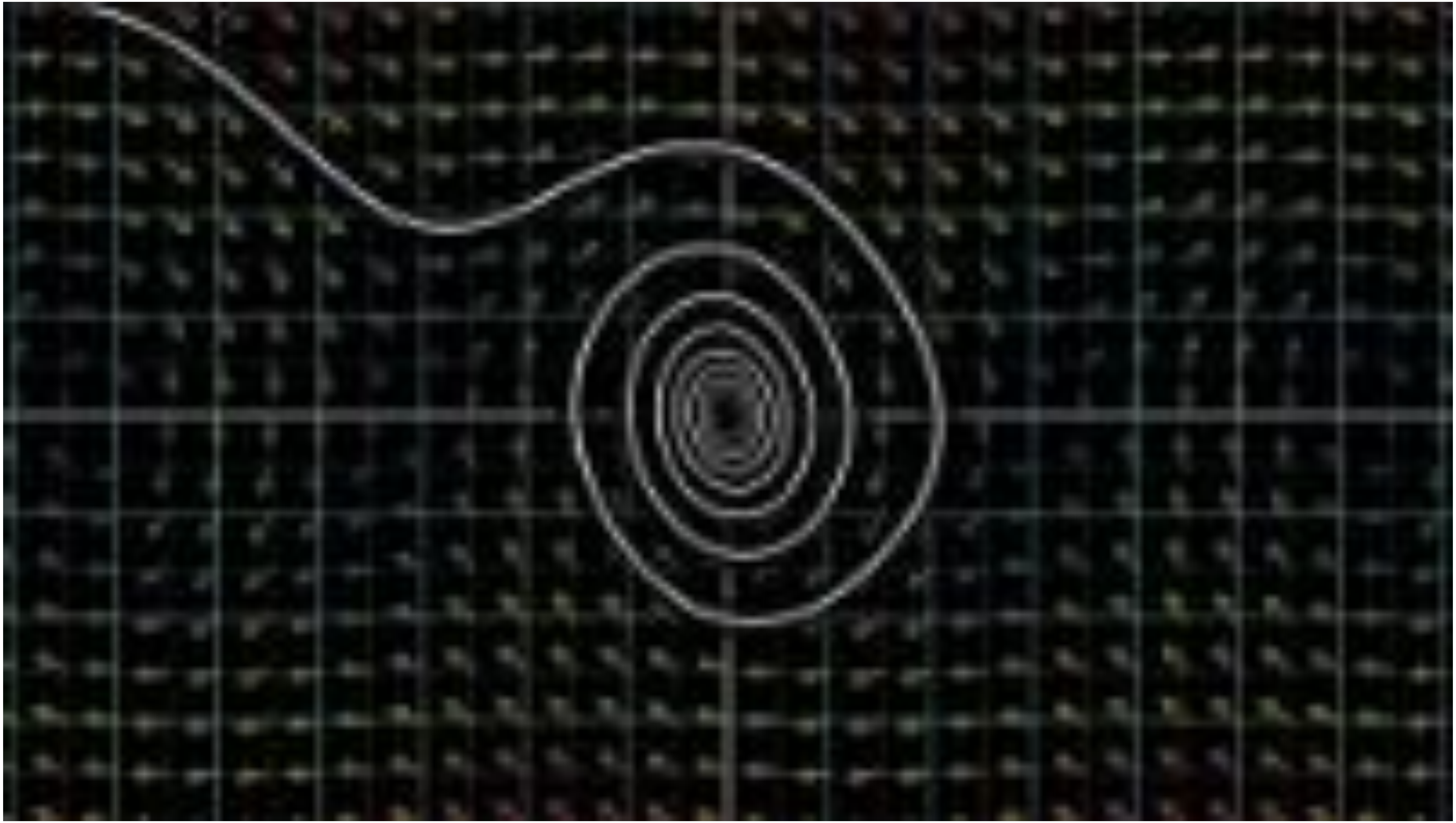
Another math remainder



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Differential equations

A differential equation is an equation relating unknown functions and their derivatives.

Example:

$$\frac{df(x)}{dx} - f(x) = 0$$

What's $f(x)$ satisfying this equation?

Differential equations

More examples:

$$\frac{d^2\mathbf{r}}{dt^2} = \frac{\mathbf{F}}{m}$$ Newton's second law

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$ Schrödinger equation

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0} \qquad \nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \qquad \nabla \times \mathbf{B} = \mu_0 \left(\varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \mathbf{J} \right)$$

Maxwell equations

en.wikipedia.org/wiki/List_of_named_differential_equations

`Back to the simple example:

$$\frac{df(x)}{dx} - f(x) = 0$$

$$\frac{df(x)}{dx} = f(x) \qquad \rightarrow \frac{df(x)}{f(x)} = dx$$

$$\int_{f_0}^{f(x)} \frac{df'}{f'} = \int_{x_0}^{x} x'\,dx' \qquad \rightarrow \ln\left(f(x)\right) - \ln\left(f_0\right) = x - x_0$$

$$\ln\left(\frac{f(x)}{f_0}\right) = x - x_0$$

$$\frac{f(x)}{f_0} = e^{x-x_0}$$

$$\rightarrow f(x) = f_0 e^{x-x_0}$$

Most time, we can't get an analytical solution.
We must resort to numerical approximations.

For example

$$\frac{df(x)}{dx} = f(x) \qquad \rightarrow \frac{\Delta f(x)}{\Delta x} = f(x)$$

$$\frac{f(x+\Delta x) - f(x)}{\Delta x} = f(x)$$

$$f(x+\Delta x) = f(x)(1+\Delta x)$$

$$f(x+\Delta x) = f(x)(1+\Delta x)$$

Suppose

$$f(0) = 1$$

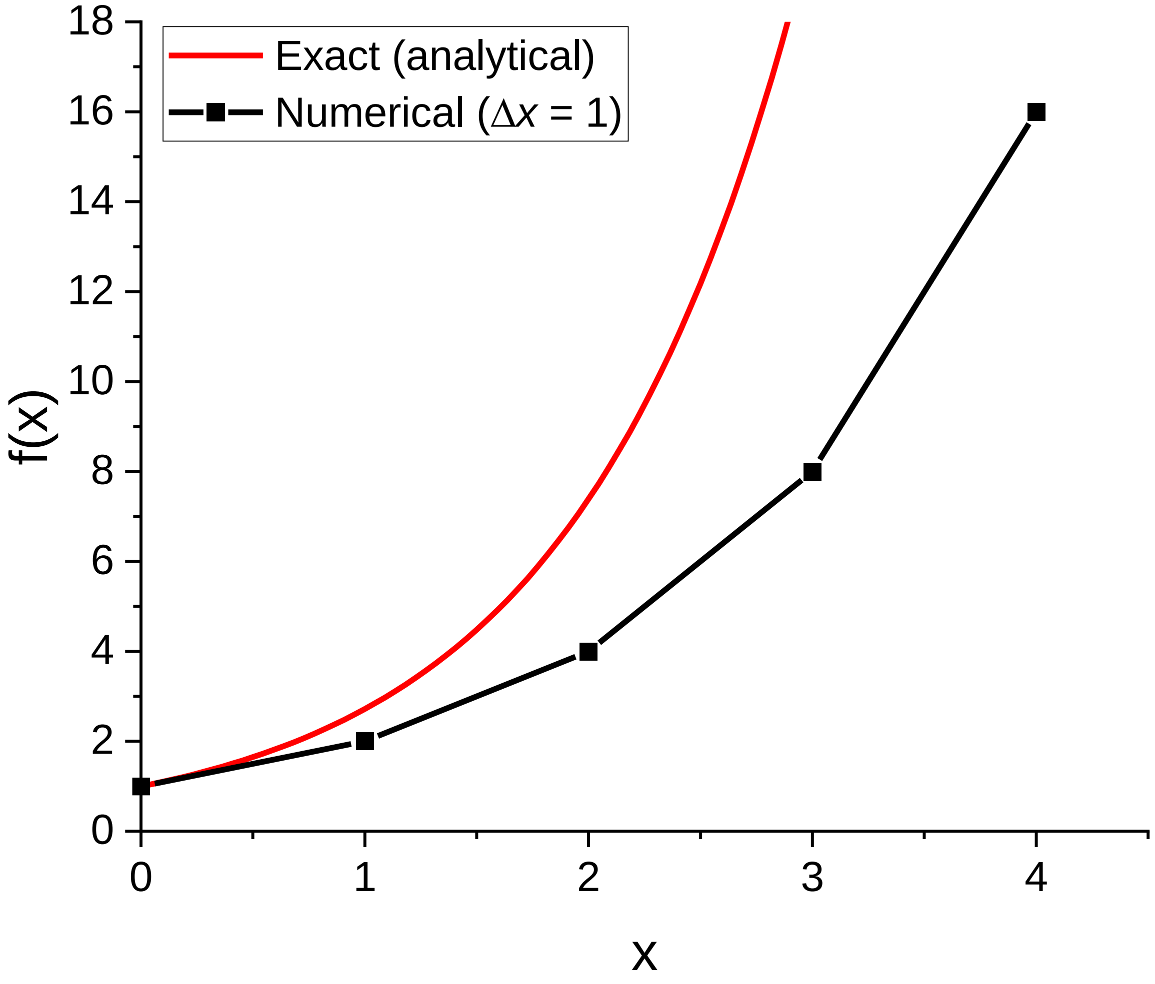
$$\Delta x = 1$$

$$f(0+\Delta x) = f(1) = 1(1+1) = 2$$

$$f(1+\Delta x) = f(2) = 2(1+1) = 4$$

$$f(2+\Delta x) = f(3) = 4(1+1) = 8$$

$$f(3+\Delta x) = f(4) = 8(1+1) = 16$$



EOM integration

Given the initial conditions $\mathbf{R}_0$ and $\mathbf{v}_0$, we want to integrate

$$M_\alpha \frac{d^2\mathbf{R}_\alpha}{dt^2} = \mathbf{F}_\alpha$$

where

$$\mathbf{F}_\alpha = -\nabla_\alpha E\left(\mathbf{R}(t)\right) + \mathbf{F}^{(e)}$$

$E(\mathbf{R})$ is the Born-Oppenheimer potential energy and $\mathbf{F}^{(e)}$ are the external forces.

One of the most popular methods to integrate this differential equation is the Velocity Verlet.

Note that

$$M_\alpha \frac{d^2\mathbf{R}_\alpha}{dt^2} = \mathbf{F}_\alpha$$

means

$$M_\alpha \left(\frac{d^2x_\alpha}{dt^2}, \frac{d^2y_\alpha}{dt^2}, \frac{d^2z_\alpha}{dt^2} \right) = \left(F_{x,\alpha}, F_{y,\alpha}, F_{z,\alpha} \right)$$

or yet ...

$$
\begin{bmatrix}
M_1 \frac{d^2 x_1}{dt^2} & M_1 \frac{d^2 y_1}{dt^2} & M_1 \frac{d^2 z_1}{dt^2} \\
M_2 \frac{d^2 x_2}{dt^2} & M_2 \frac{d^2 y_2}{dt^2} & M_2 \frac{d^2 z_2}{dt^2} \\
\vdots & \vdots & \vdots \\
M_N \frac{d^2 x_N}{dt^2} & M_N \frac{d^2 y_N}{dt^2} & M_N \frac{d^2 z_N}{dt^2}
\end{bmatrix}
=
\begin{bmatrix}
F_{1,x} & F_{1,y} & F_{1,z} \\
F_{2,x} & F_{2,y} & F_{2,z} \\
\vdots & \vdots & \vdots \\
F_{N,x} & F_{N,y} & F_{N,z}
\end{bmatrix}
$$

where *N* is the number of nuclei.

Thus, we must solve 3*N* coupled differential equations of type

$$
M_\alpha \frac{d^2 x_{\alpha,i}}{dt^2} = F_{\alpha,i} \quad \left(x_1 = x, x_2 = y, x_3 = z \right)
$$

Simple example

1 particle in 1 dimension

$$M \frac{d^2 x}{dt^2} = F$$

Constant force

$$F = -Mg$$

Initial conditions

$$x(0) = x_0; \quad v(0) = v_0$$

Solution

$$x(t) = x_0 + v_0 t - \frac{1}{2} g t^2$$

Velocity Verlet

For each nucleus α and coordinate x_i ($x_1 = x$, $x_2 = y$, $x_3 = z$):

$$a_{\alpha,i}(t) = \frac{1}{M_\alpha}\left(-\frac{\partial E(\mathbf{R}(t))}{\partial x_{\alpha,i}} + F_{\alpha,i}^{(e)}\right)$$

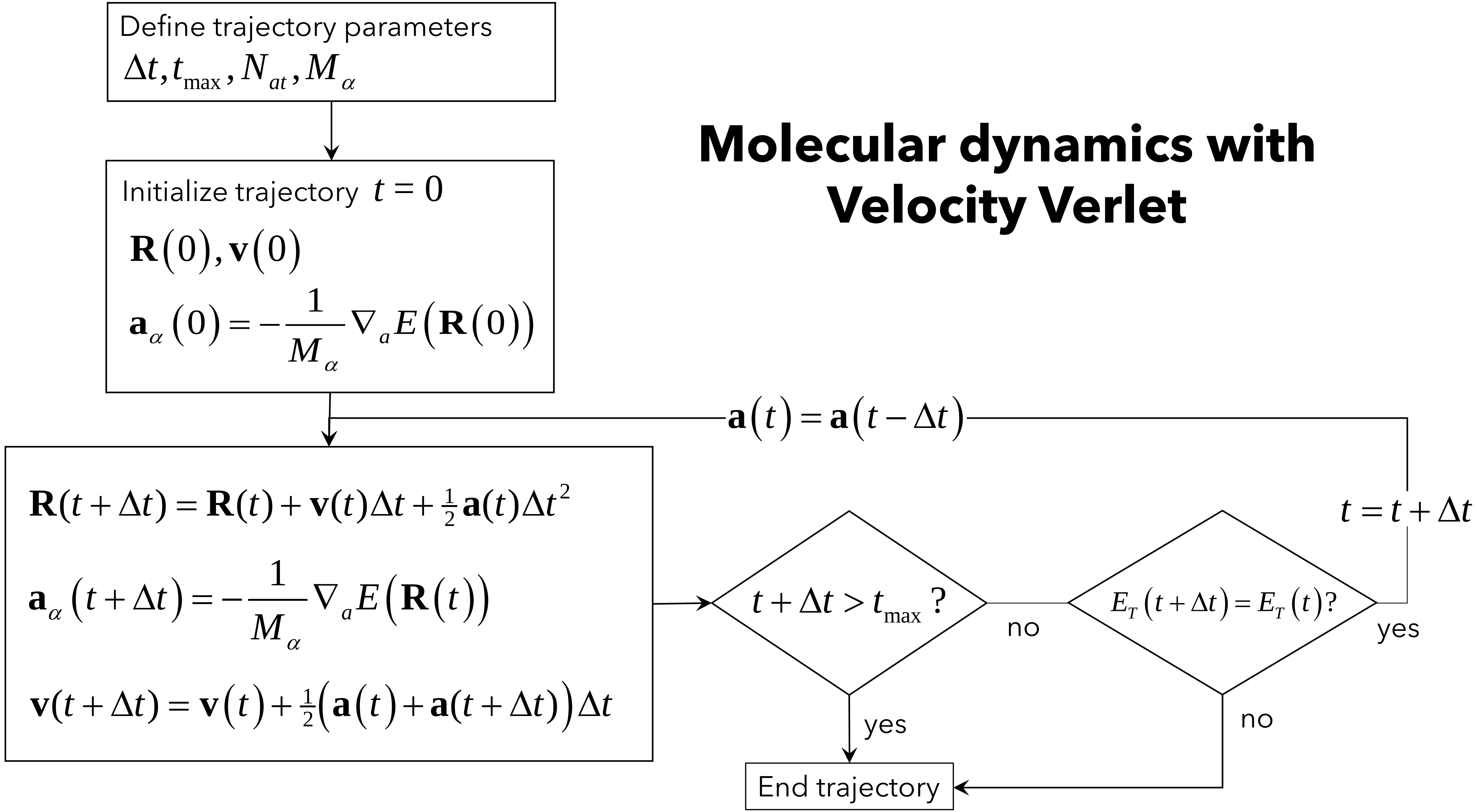
$$x_{\alpha,i}(t+\Delta t) = x_{\alpha,i}(t) + v_{\alpha,i}(t)\Delta t + \tfrac{1}{2}a_{\alpha,i}(t)\Delta t^2$$

$$a_{\alpha,i}(t+\Delta t) = \frac{1}{M_\alpha}\left(-\frac{\partial E(\mathbf{R}(t+\Delta t))}{\partial x_{\alpha,i}} + F_{\alpha,i}^{(e)}\right)$$

$$v_{\alpha,i}(t+\Delta t) = v_{\alpha,i}(t) + \tfrac{1}{2}\left(a_{\alpha,i}(t) + a_{\alpha,i}(t+\Delta t)\right)\Delta t$$

Swope et al. J. Chem. Phys. **76**, 637 (1982)
For a recent method: Predescu *et al. Mol Phys* **2012**, *110*, 967

Molecular dynamics with Velocity Verlet



Integration step size

Time-step

Table 1 Some typical vibrational modes[a]

Vibrational mode	Wavelength of absorption [cm^{-1}] ($1/\lambda$)	Absorption frequency [s^{-1}] ($\nu = c/\lambda$)	Period [fs] ($1/\nu$)	Period/π [fs]
O−H stretch	3200–3600	1.0×10^{14}	9.8	3.1
N−H stretch				
C−H stretch	3000	9.0×10^{13}	11.1	3.5
O−C−O asymmetric stretch	2400	7.2×10^{13}	13.9	4.5
C≡C, C≡N stretch	2100	6.3×10^{13}	15.9	5.1
C=O (carbonyl) stretch	1700	5.1×10^{13}	19.6	6.2
C=C stretch				
H−O−H bend	1600	4.8×10^{13}	20.8	6.4
C−N−H bend	1500	4.5×10^{13}	22.2	7.1
H−N−H bend				
C=C (aromatic) stretch				
C−N stretch (amines)	1250	3.8×10^{13}	26.2	8.4
Water Libration (rocking)	800	2.4×10^{13}	41.7	13
O−C−O bending	700	2.1×10^{13}	47.6	15
C=C−H bending (alkenes)				
C=C−H bending (aromatic)				

[a]All values are approximate; a range is associated with each motion depending on the system. The value of $c = 3.00 \times 10^{10}$ cm s^{-1}. The last column indicates the timestep limit for leap-frog stability for a harmonic oscillator: $\Delta t < 2/\omega = 2/(2\pi\nu)$.

Schlick, Barth and Mandziuk, *Annu. Rev. Biophys. Struct*. **1997**, *26*, 181

Time-step

Table 1 Some typical vibrational modes[a]

Vibrational mode	Wavelength of absorption [cm^{-1}] ($1/\lambda$)	Absorption frequency [s^{-1}] ($\nu = c/\lambda$)	Period [fs] ($1/\nu$)	Period/π [fs]
O—H stretch	3200–3600	1.0×10^{14}	9.8	3.1
N—H stretch				
C—H stretch	3000	9.0×10^{13}	11.1	3.5

Time step should not be larger than 1 fs ($1/10v$).

Δt = 0.5 fs assures a good level of conservation of energy.

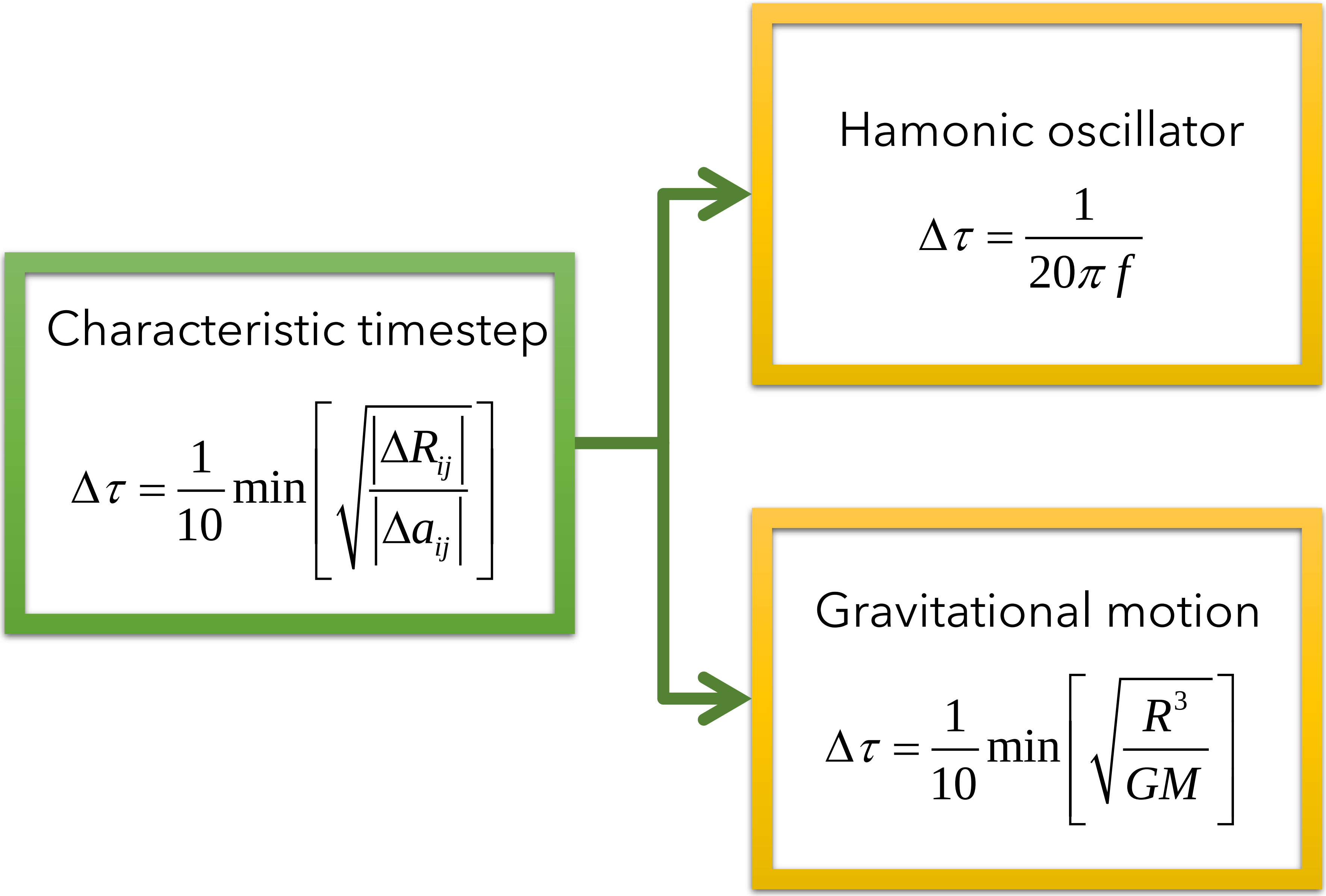
Exceptions requiring shorter steps:
- Dynamics close to a conical intersection
- Dissociation processes
- Long timescale

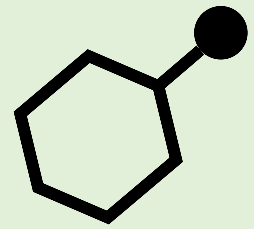
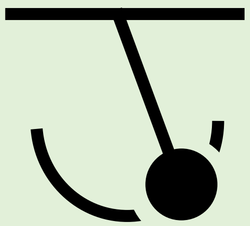
10 ps/0.1 fs = 100,000 time steps

Characteristic timestep

$$\Delta\tau = \frac{1}{10}\min\left[\sqrt{\frac{\left|\Delta R_{ij}\right|}{\left|\Delta a_{ij}\right|}}\right]$$

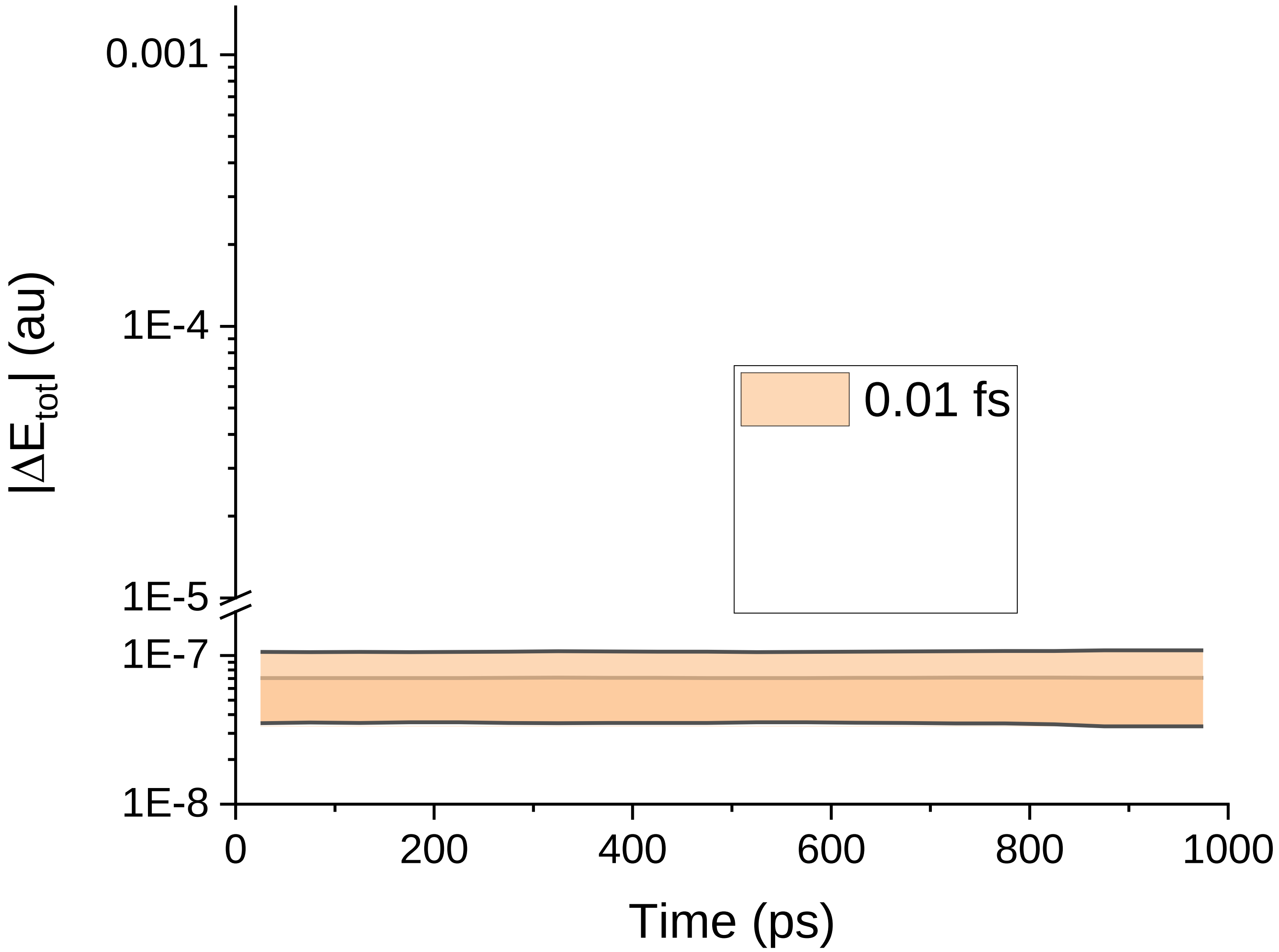
Boekholt; Zwart. *Comput Astrophys Cosmol* **2015,** *2*, 2


Characteristic timestep
$\Delta\tau = \frac{1}{10}\min\left[\sqrt{\frac{|\Delta R_{ij}|}{|\Delta a_{ij}|}}\right]$
Hamonic oscillator
$\Delta\tau = \frac{1}{20\pi f}$
Gravitational motion
$\Delta\tau = \frac{1}{10}\min\left[\sqrt{\frac{R^3}{GM}}\right]$

	$\Delta\tau = \frac{1}{20\pi f}$	$f = 3000\ \text{cm}^{-1}$	$\Delta\tau \approx 0.1\ \text{fs}$ $\tau > 10\ \text{ps}$
	$\Delta\tau = \frac{1}{20\pi f}$	$f = 1\ \text{Hz}$	$\Delta\tau \approx 0.01\ \text{s}$ $\tau > 16\ \text{min}$
	$\Delta\tau = \frac{1}{10}\min\left[\sqrt{\frac{R^3}{GM}}\right]$	*Earth orbital motion*	$\Delta\tau \approx 100\ \text{h}$ $\tau > 1100\ \text{years}$

Integration stability: time step effect

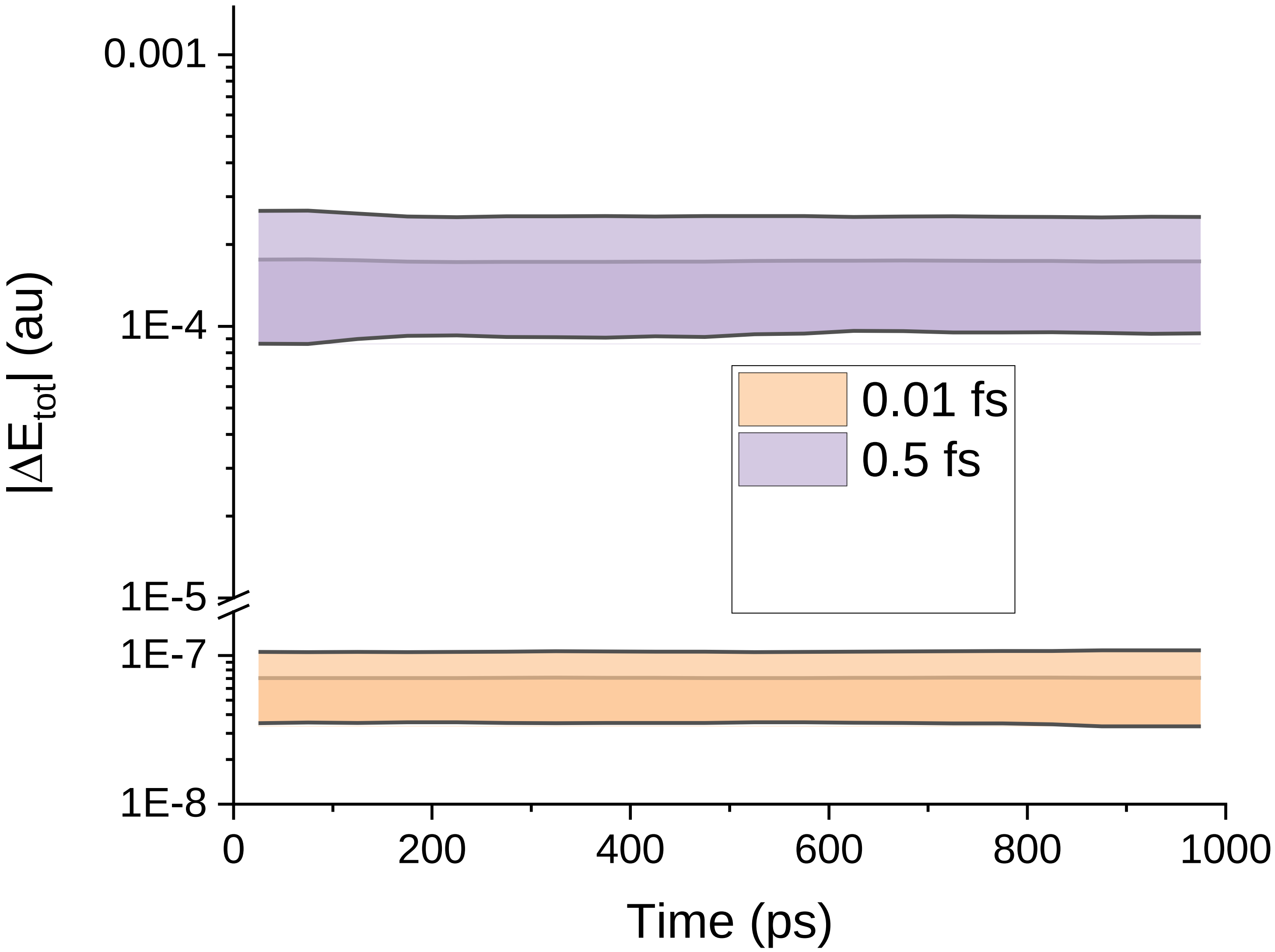
Velocity Verlet



- A-SBH 33D
- dynamics on E_2

Mukherjee, Barbatti *et al*. *Philos Trans R Soc A* **2022,** *80*, 20200382

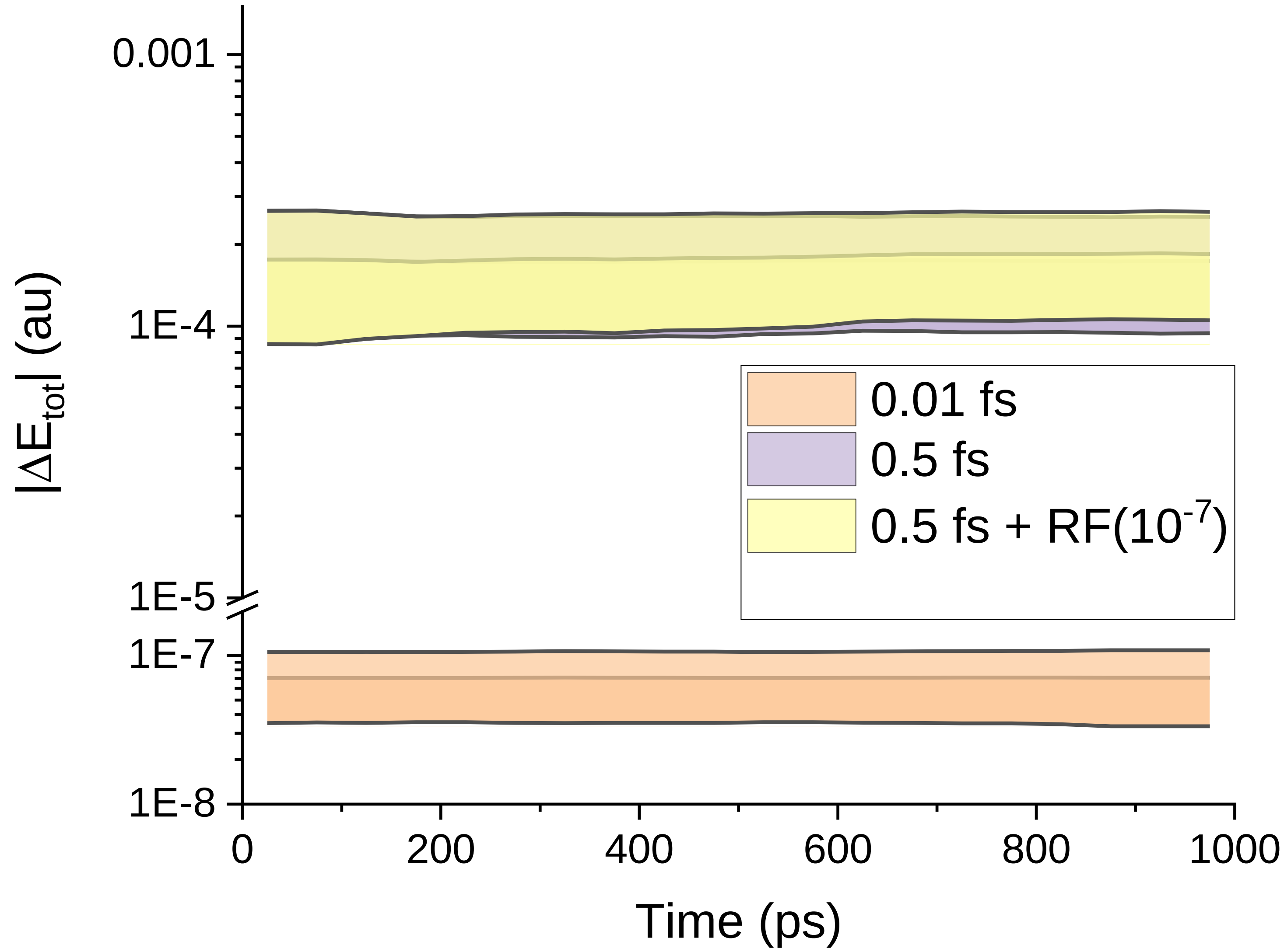
Velocity Verlet



- A-SBH 33D
- dynamics on E_2

Mukherjee, Barbatti *et al*. *Philos Trans R Soc A* **2022,** *80*, 20200382

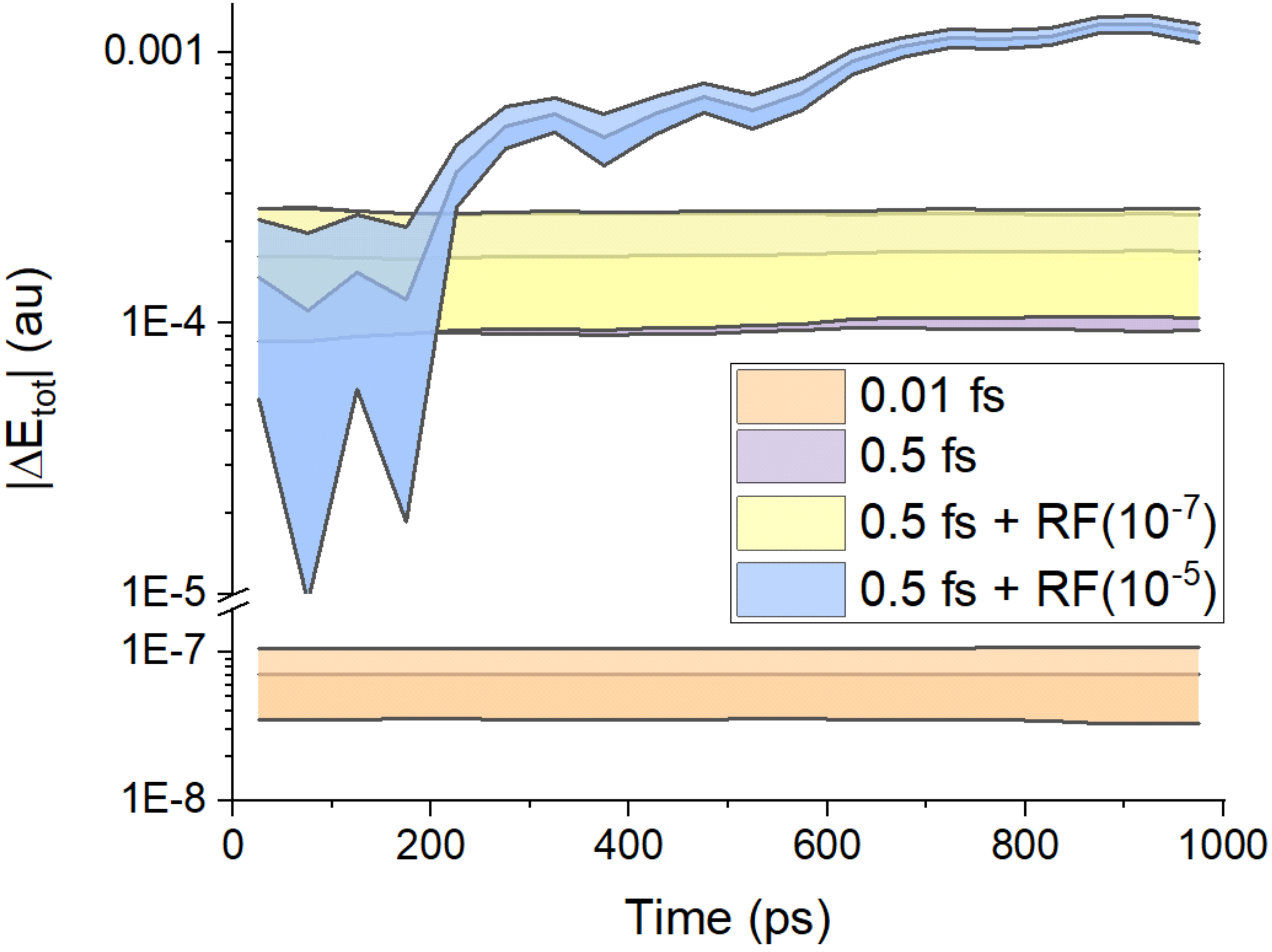
Velocity Verlet



- A-SBH 33D
- dynamics on E_2

Mukherjee, Barbatti *et al*. *Philos Trans R Soc A* **2022,** *80*, 20200382

Velocity Verlet



- A-SBH 33D
- dynamics on E_2

Mukherjee, Barbatti *et al*. *Philos Trans R Soc A* **2022,** *80*, 20200382

Velocity Verlet is a **symplectic integrator**.

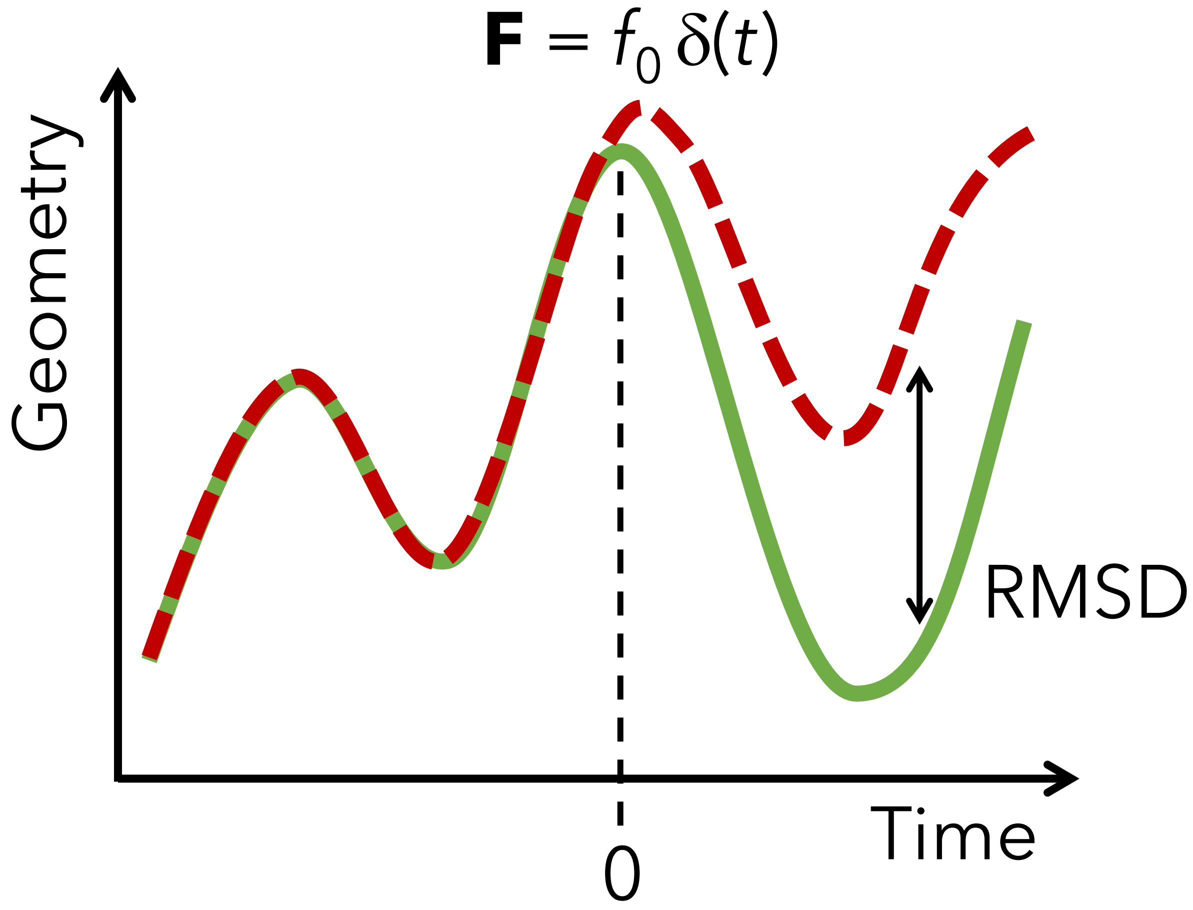
It means that it tends to conserve total energy, even when an error is introduced due to discretization (finite time steps).

Not all integrators are symplectic.
Runge-Kutta, for instance, is not symplectic, and the total energy tends to drift.

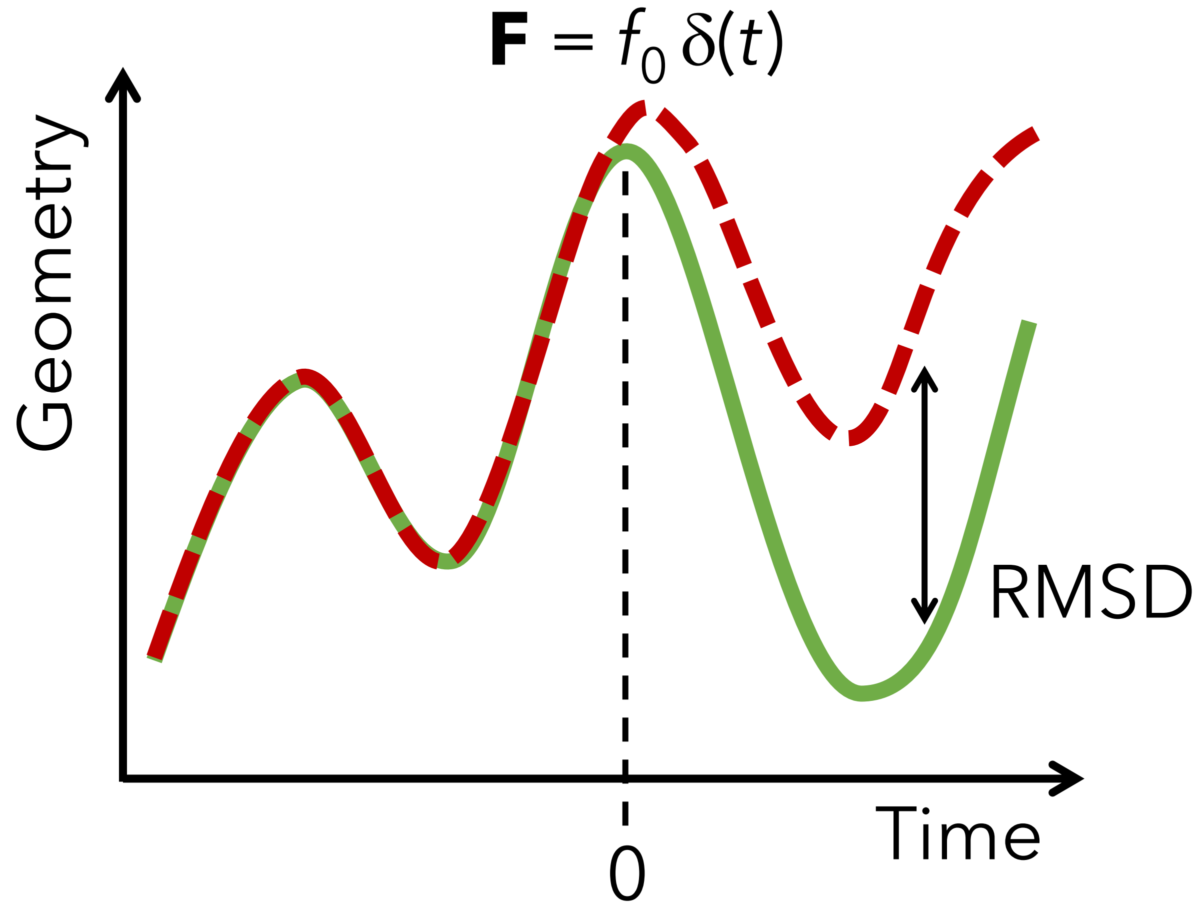
en.wikipedia.org/wiki/Symplectic_integrator

Integration stability:
gradient accuracy effect

Effect of force uncertainty



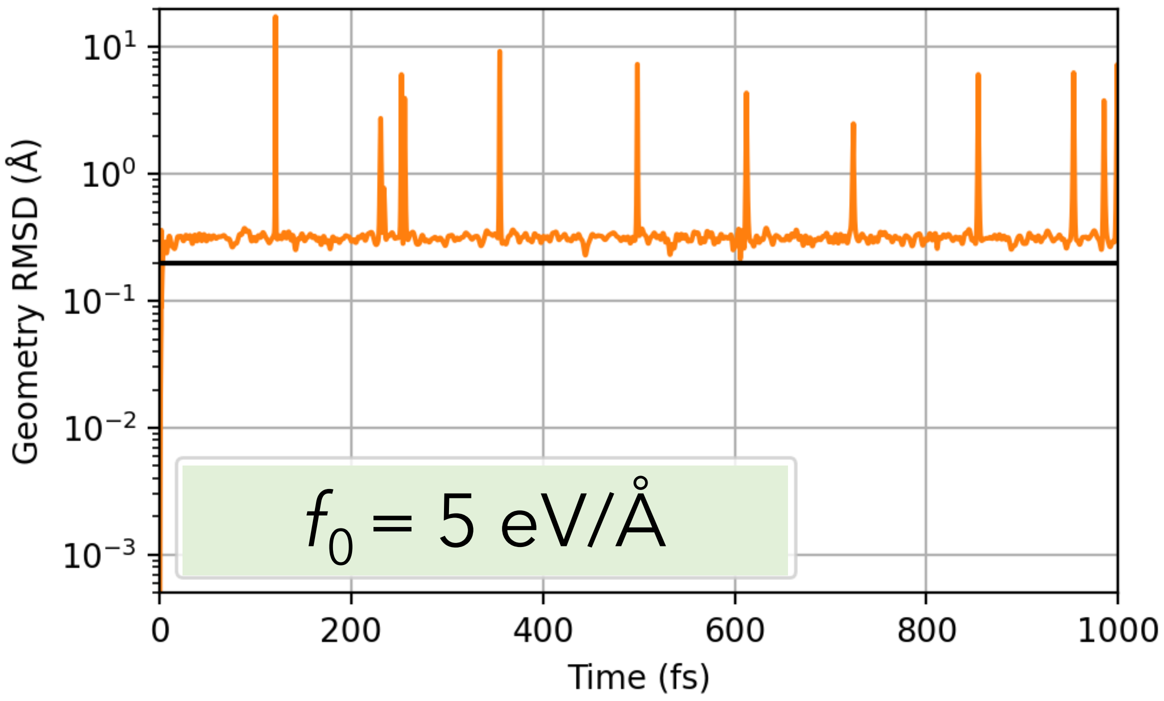
Effect of force uncertainty

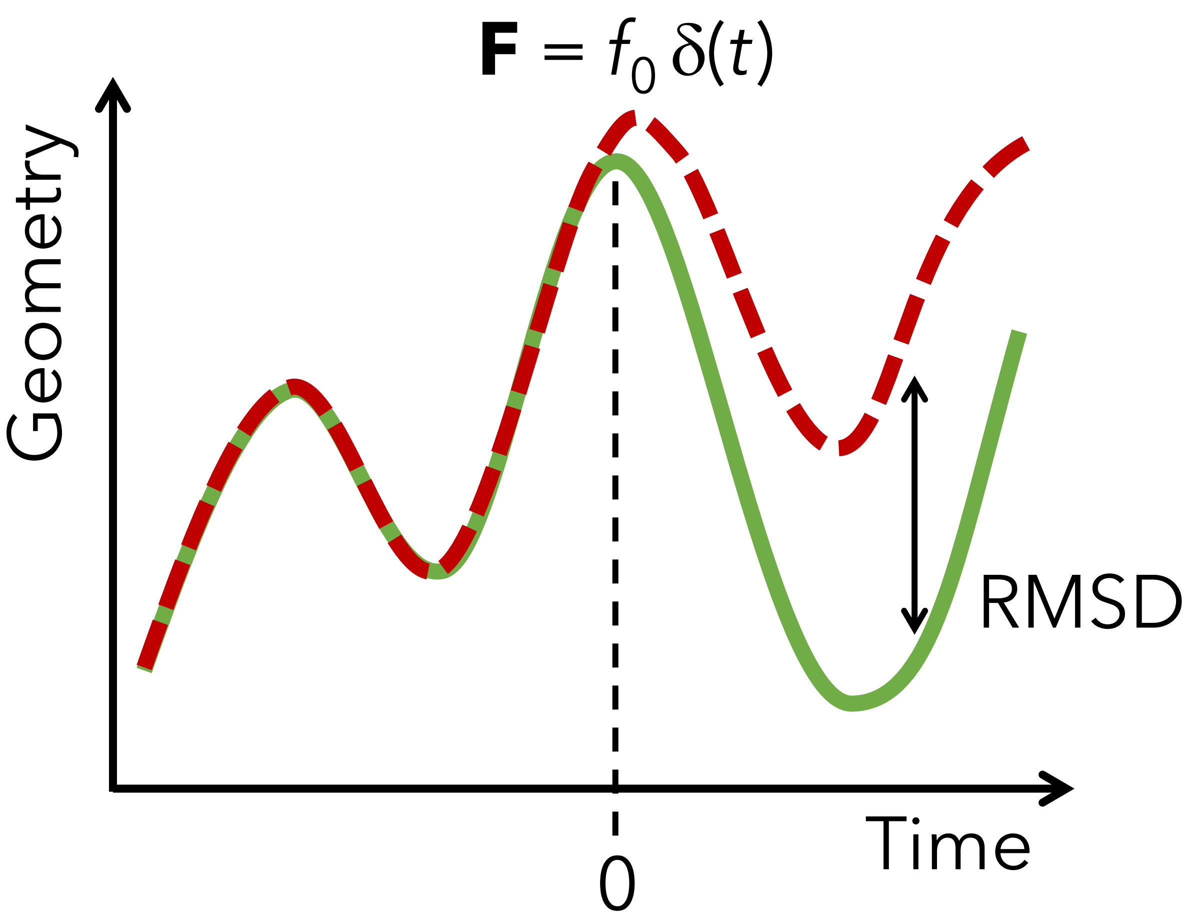


Geometrical accuracy
We want results better than 0.2 Å.

- A-SBH 33D
- dynamics on E_1

Effect of force uncertainty

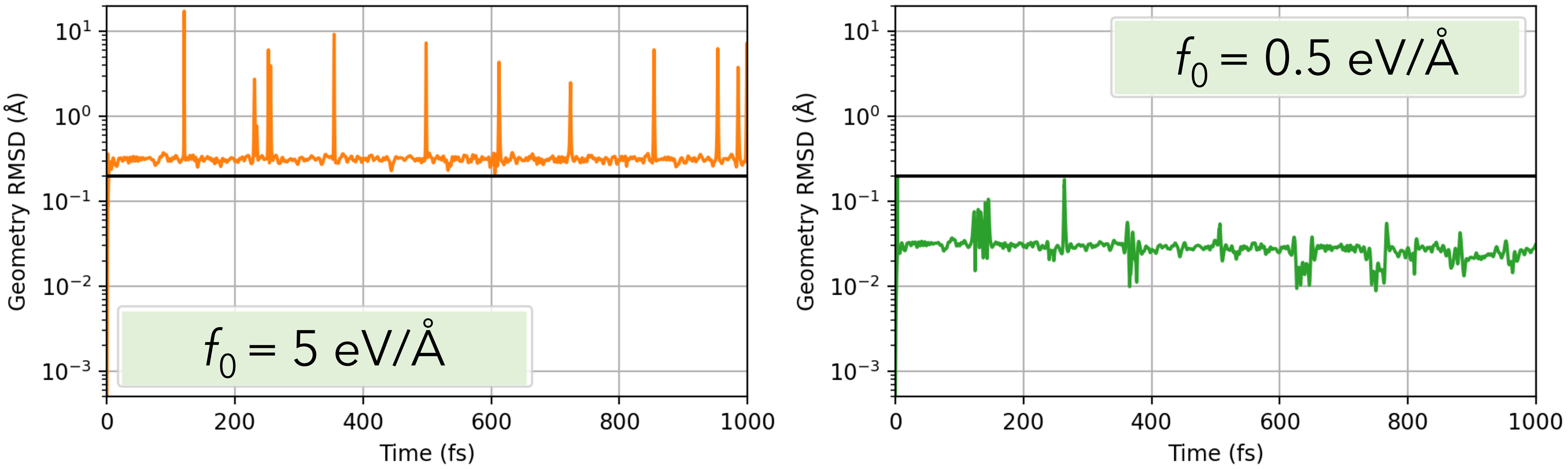




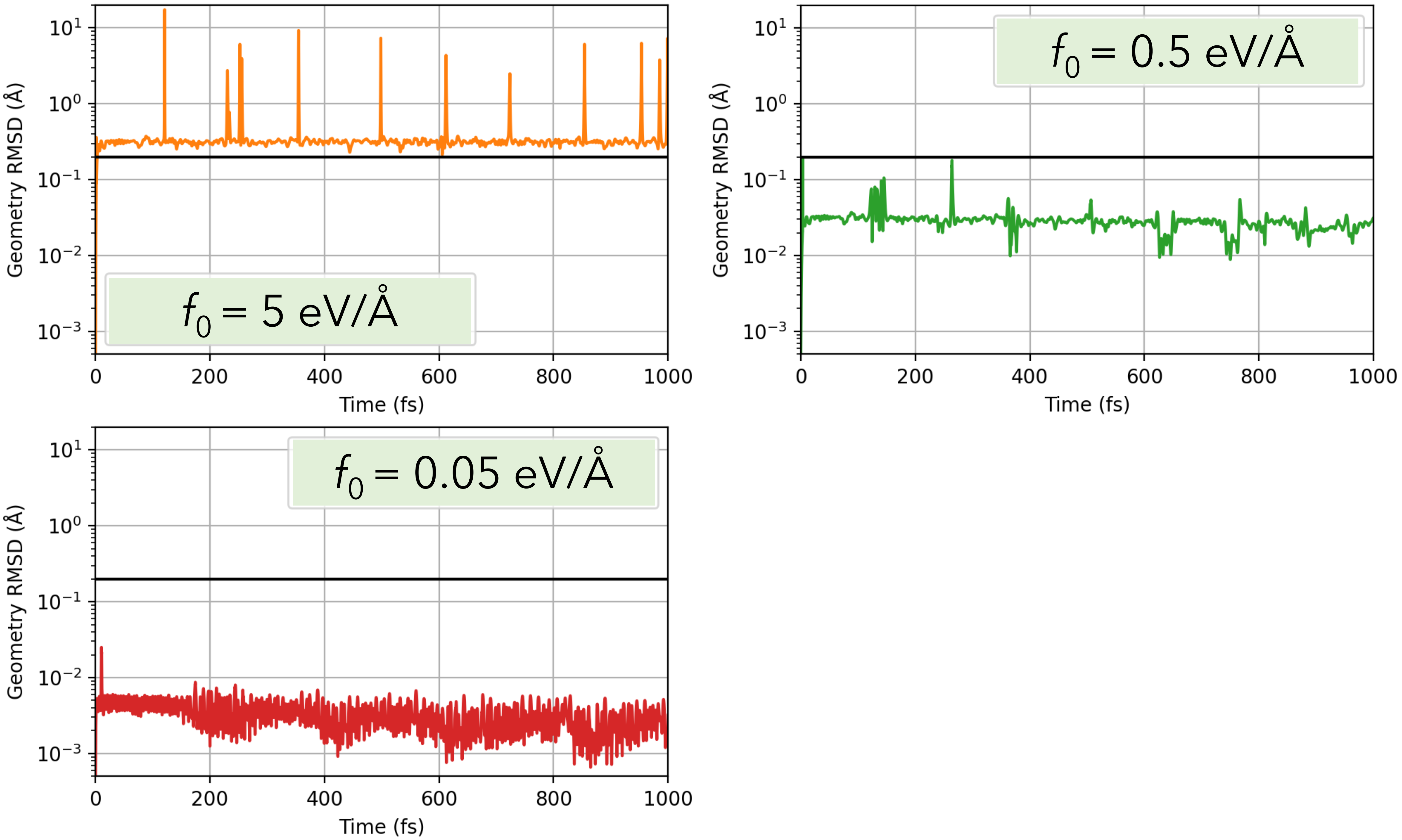
Geometrical accuracy

We want results better than 0.2 Å.

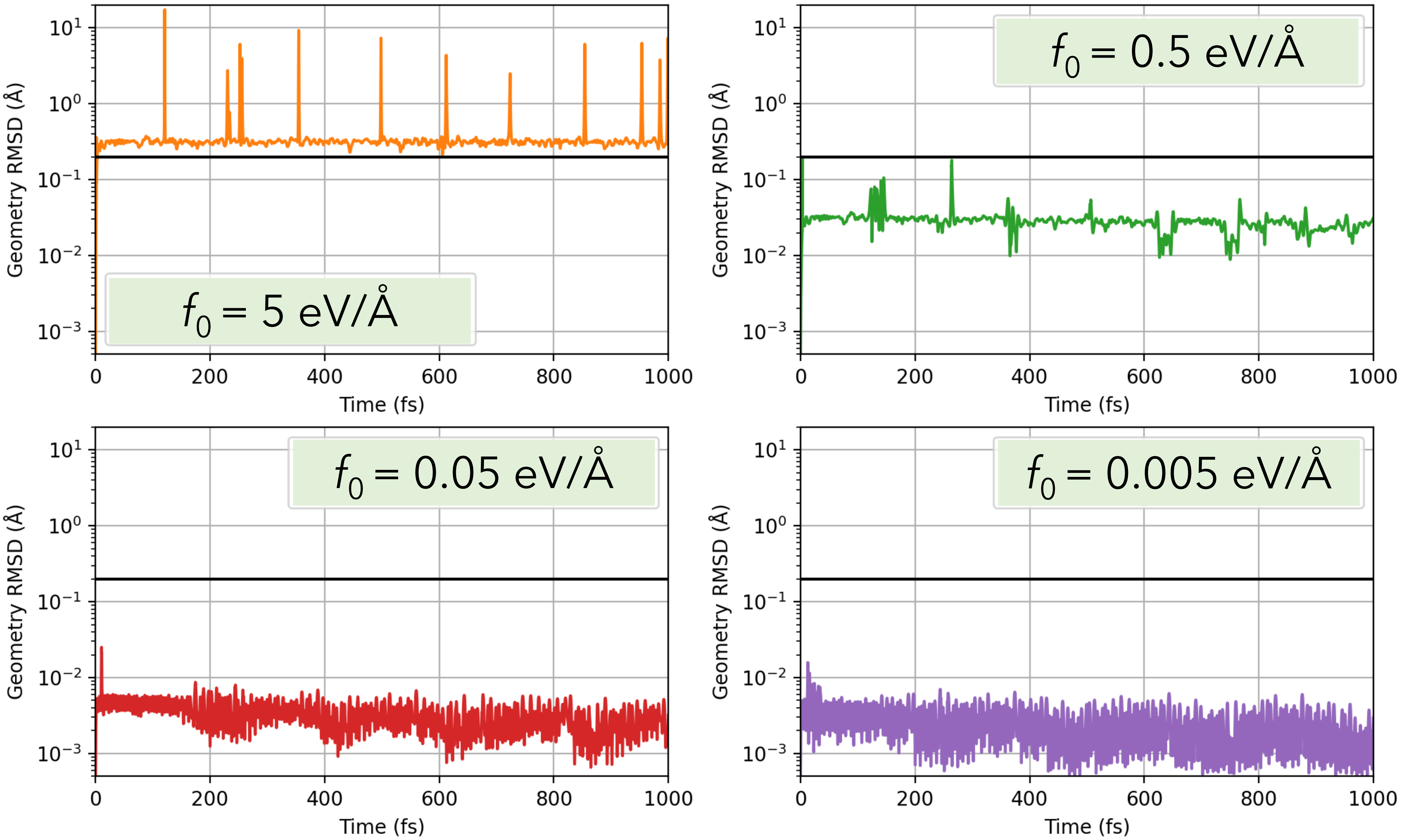
- A-SBH 33D
- dynamics on E_1



Geometry RMSD (Å)
Time (fs)
$f_0 = 5$ eV/Å
$f_0 = 0.5$ eV/Å



$f_0 = 5$ eV/Å
$f_0 = 0.5$ eV/Å
$f_0 = 0.05$ eV/Å
Geometry RMSD (Å)
Time (fs)



$f_0 = 5$ eV/Å
$f_0 = 0.5$ eV/Å
$f_0 = 0.05$ eV/Å
$f_0 = 0.005$ eV/Å
Geometry RMSD (Å)
Time (fs)
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
0
200
400
600
800
1000

We must predict forces better than
0.5 eV/Å (0.001 Hartree/Bohr)

(Maximum absolute error)

To know more:

Classical mechanics

- Goldstein, Classical mechanics. **1980**. Ch 1
- en.wikipedia.org/wiki/Verlet_integration

Available for download at:
amubox.univ-amu.fr/s/xXAiMZrDPb9RMRX
Ask me for the password.

Demonstration of equation

$$\mathbf{L} = \sum_i \mathbf{r}_i' \times \mathbf{p}_i' + \mathbf{R} \times \mathbf{P}$$

$$\mathbf{r}_i = \mathbf{r}_i' + \mathbf{R}$$

$$\frac{d\mathbf{r}_i}{dt} = \frac{d\mathbf{r}_i'}{dt} + \frac{d\mathbf{R}}{dt}$$

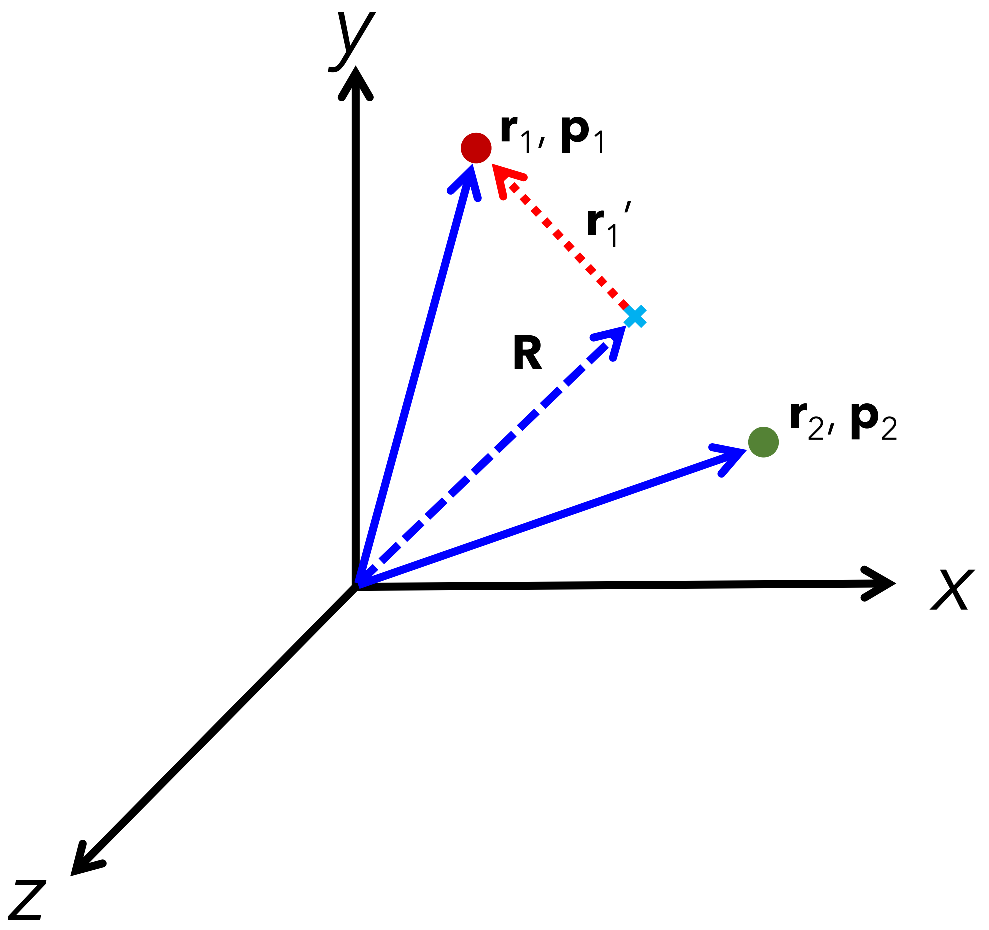
$$\mathbf{v}_i = \mathbf{v}_i' + \mathbf{v}$$

$$\mathbf{r}_i' = \mathbf{r}_i - \mathbf{R}$$

$$\sum_i m_i \mathbf{r}_i' = \sum_i m_i \mathbf{r}_i - \sum_i m_i \mathbf{R}$$

$$\sum_i m_i \mathbf{r}_i' = \sum_i m_i \mathbf{r}_i - M\mathbf{R}$$

$$= \sum_i m_i \mathbf{r}_i - M\left(\frac{1}{M}\sum_i m_i \mathbf{r}_i\right) = 0$$



$$
\begin{aligned}
\mathbf{L} &= \sum_i \mathbf{r}_i \times \mathbf{p}_i \\
&= \sum_i \left(\mathbf{r}_i' + \mathbf{R}\right) \times m_i \left(\mathbf{v}_i' + \mathbf{v}\right) \\
&= \sum_i \mathbf{r}_i' \times m_i \mathbf{v}_i' + \left(\sum_i m_i \mathbf{r}_i'\right) \times \mathbf{v} + \mathbf{R} \times \left(\sum_i m_i \mathbf{v}_i'\right) + \mathbf{R} \times \left(\sum_i m_i\right) \mathbf{v} \\
&= \sum_i \mathbf{r}_i' \times m_i \mathbf{v}_i' + \left(\sum_i m_i \mathbf{r}_i'\right) \times \mathbf{v} + \mathbf{R} \times \left(\sum_i m_i \mathbf{v}_i'\right) + \mathbf{R} \times M\mathbf{v} \\
&= \sum_i \mathbf{r}_i' \times \mathbf{p}_i' + \underbrace{\left(\sum_i m_i \mathbf{r}_i'\right)}_{0} \times \mathbf{v} + \mathbf{R} \times \underbrace{\left(\sum_i m_i \mathbf{v}_i'\right)}_{0} + \mathbf{R} \times \mathbf{P}
\end{aligned}
$$

$$
\mathbf{L} = \sum_i \mathbf{r}_i' \times \mathbf{p}_i' + \mathbf{R} \times \mathbf{P}
$$

Demonstration of equation

$$T = \frac{1}{2} M \mathbf{v}^2 + \frac{1}{2} \sum_i m_i \mathbf{v}_i'^2$$

We check the total kinetic energy like we did for angular momentum:

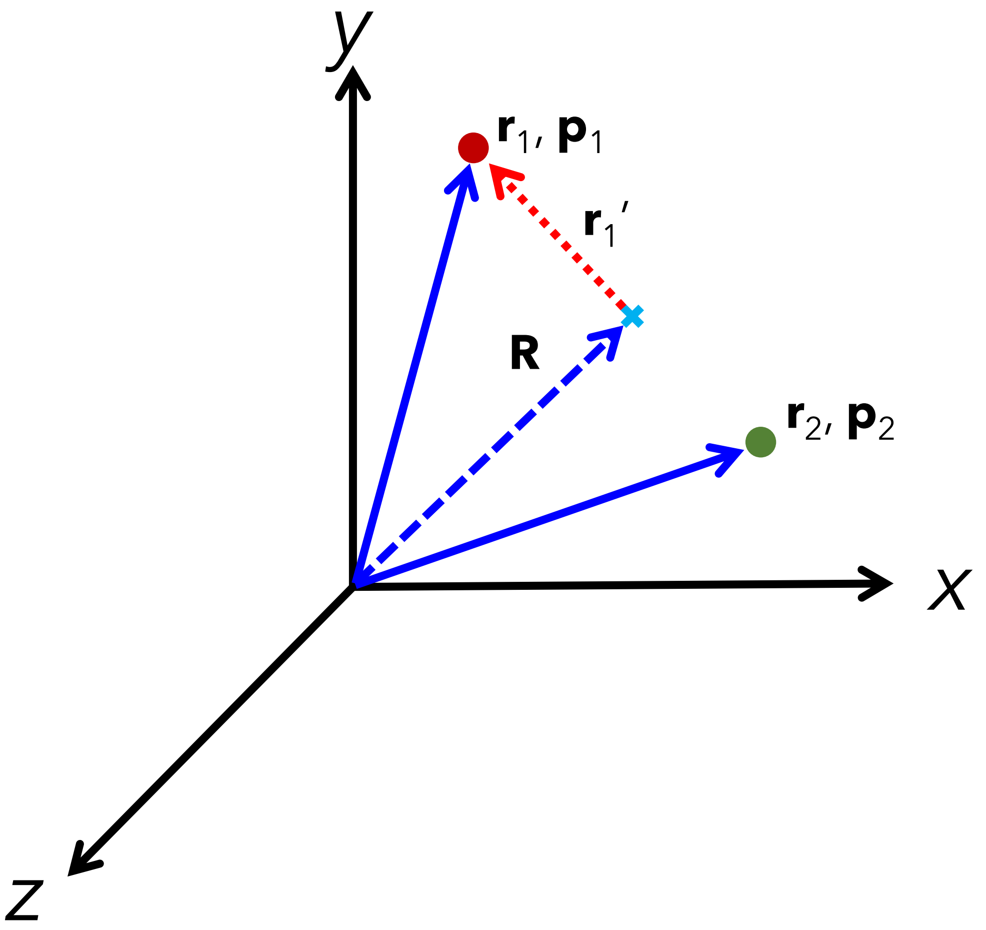
$$T = \sum_i \frac{1}{2} m_i \mathbf{v}_i^2$$

$$= \sum_i \frac{1}{2} m_i \left(\mathbf{v} + \mathbf{v}_i' \right)^2$$

$$= \sum_i \frac{1}{2} m_i \left(\mathbf{v}^2 + 2\mathbf{v} \cdot \mathbf{v}_i' + \mathbf{v}_i'^2 \right)$$

$$= \frac{1}{2} M\mathbf{v}^2 + \mathbf{v} \cdot \underbrace{\sum_i m_i \mathbf{v}_i'}_{0} + \frac{1}{2} \sum_i m_i \mathbf{v}_i'^2$$

$$= \frac{1}{2} M\mathbf{v}^2 + \frac{1}{2} \sum_i m_i \mathbf{v}_i'^2$$



Demonstration of equations

$$W_{12} = T_B - T_A$$

$$W_{12} = V_A - V_B$$

The work of a system of particles is the variation of their kinetic energy

$$W_{AB} = \sum_i \int_A^B \mathbf{F}_i \cdot d\mathbf{s}_i = \sum_i \int_A^B m_i \frac{d\mathbf{v}_i}{dt} \cdot \mathbf{v}_i dt$$

$$= \sum_i \left(T_{i,B} - T_{i,A} \right)$$

$$= T_B - T_A$$

The work in terms of potential energies

$$W_{12} = \sum_i \int_A^B \mathbf{F}_i \cdot d\mathbf{s}_i$$

$$= \sum_i \int_A^B \mathbf{F}_i^{(e)} \cdot d\mathbf{s}_i + \sum_{\substack{i,j \\ j \neq i}} \int_A^B \mathbf{F}_{ji} \cdot d\mathbf{s}_i$$

If the external forces are conservative

$$\sum_i \int_A^B \mathbf{F}_i^{(e)} \cdot d\mathbf{s}_i = -\sum_i \int_A^B \nabla_i V_i \cdot d\mathbf{s}_i = \sum_i \left(V_{i,A} - V_{i,B} \right)$$

If the internal forces are conservative and central

$$\mathbf{F}_{ji} = -\nabla V_{ij}\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right)$$

Then the work is

$$\sum_{\substack{i,j \\ j\neq i}} \int_A^B \mathbf{F}_{ji} \cdot d\mathbf{s}_i = -\sum_{\substack{i,j \\ j\neq i}} \int_A^B \nabla_i V_{ji} \cdot d\mathbf{s}_i$$

$N = 2$

$$-\sum_{\substack{i,j \\ j\neq i}} \int_A^B \nabla_i V_{ji} \cdot d\mathbf{s}_i = -\int_A^B \nabla_1 V_{21} \cdot d\mathbf{s}_1 - \int_A^B \nabla_2 V_{12} \cdot d\mathbf{s}_2$$

$$d\mathbf{s}_1 - d\mathbf{s}_2 = d\mathbf{r}_1 - d\mathbf{r}_2 = d\left(\mathbf{r}_1 - \mathbf{r}_2\right) = d\mathbf{r}_{12}$$

$$\nabla_1 V_{12} = -\nabla_2 V_{12} = \nabla_{12} V_{12}$$

$$= -\int_A^B \nabla_{12} V_{12} \cdot d\mathbf{r}_{12}$$

$$= V_{12,A} - V_{12,B}$$

The work is

$$
\begin{aligned}
W_{12} &= \sum_i \int_A^B \mathbf{F}_i \cdot d\mathbf{s}_i \\
&= \sum_i \int_A^B \mathbf{F}_i^{(e)} \cdot d\mathbf{s}_i + \sum_{\substack{i,j \\ j\neq i}} \int_A^B \mathbf{F}_{ji} \cdot d\mathbf{s}_i \\
&= \sum_i \left(V_{i,A} - V_{i,B}\right) + \sum_{ij} \left(V_{ij,A} - V_{ij,B}\right) \\
&= V_A - V_B
\end{aligned}
$$