Symplectic Molecular Dynamics

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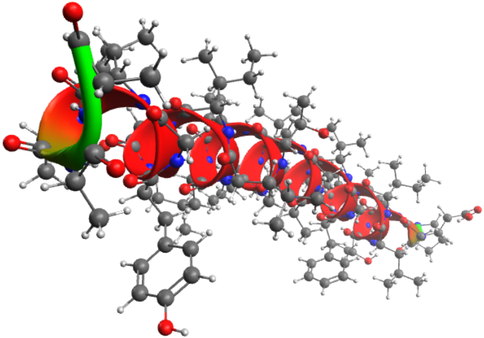
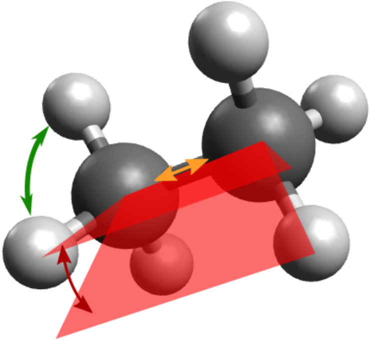
Molecules

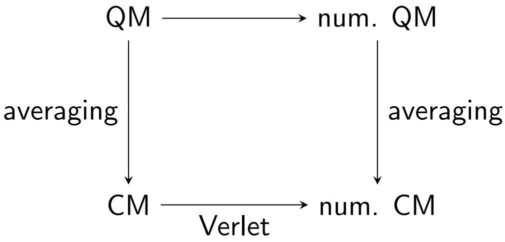


Force Fields



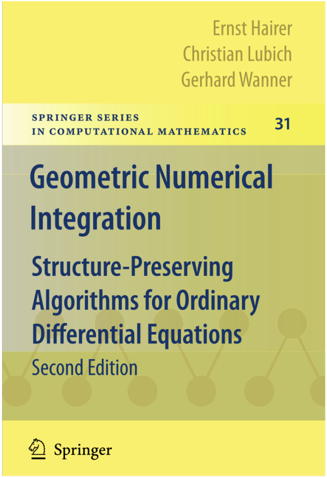
Classical Mechanics vs. Quantum Mechanics

At least the following diagram commutes asymptotically. . .



[HLW06, VII.6.4]

Symplectic Numerical Integration



Classical Molecular Dynamics

For a total energy of the form

$$\mathcal{H} = E_{\text{kin}}(\mathbf{p}) + E_{\text{pot}}(\mathbf{q}),$$

we want to solve the associated Hamilton system

$$\begin{cases} \dot{\mathbf{q}} = \nabla_{\mathbf{p}} \mathcal{H}, \\ \dot{\mathbf{p}} = -\nabla_{\mathbf{q}} \mathcal{H}. \end{cases}$$

Symplectic Structure of the Hamilton System

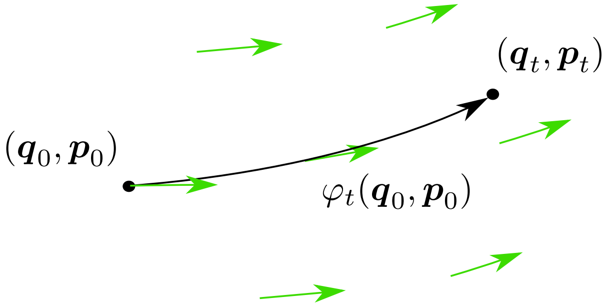
We can rewrite the Hamiltion system as

$$\dot{\mathbf{y}} = J^{-1} \circ \nabla_{\mathbf{y}} \mathcal{H}(\mathbf{y})$$

where $\mathbf{y} = (\mathbf{q}, \mathbf{p})$ and

$$J = \begin{pmatrix} 0 & I \\ -I & 0 \end{pmatrix} \in \mathbb{R}^{2n \times 2n}.$$

Let φ_t denote the flow of the Hamilton system.



Sum of Projected Areas

We define the differential 2-form $\omega = \mathrm{d}\mathbf{p} \wedge \mathrm{d}\mathbf{q}$.

Let $\boldsymbol{\xi} = (\boldsymbol{\xi}^q, \boldsymbol{\xi}^p), \boldsymbol{\eta} = (\boldsymbol{\eta}^q, \boldsymbol{\eta}^p) \in \mathrm{T}_{(\mathbf{q},\mathbf{p})}\,\mathbb{R}^{2dN}$ be two tangent vectors at $(\mathbf{q}, \mathbf{p})$, then the explicit formula for ω is given by

$$\omega(\boldsymbol{\xi}, \boldsymbol{\eta})\,\Big|_{(\mathbf{q},\mathbf{p})} = \sum_{j=1}^{dN} \det \begin{pmatrix} \xi_j^q & \eta_j^q \\ \xi_j^p & \eta_j^p \end{pmatrix} = \sum_{j=1}^{dN} \xi_j^q \eta_j^p - \xi_j^p \eta_j^q .$$

In matrix notation we get

$$\omega(\boldsymbol{\xi}, \boldsymbol{\eta}) = \boldsymbol{\xi}^T J \boldsymbol{\eta}, \quad \text{where } J = \begin{pmatrix} 0 & I \\ -I & 0 \end{pmatrix}.$$

Symplectic Mappings

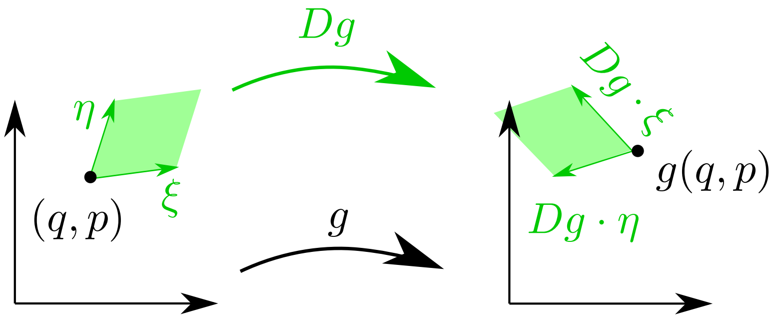
Definition (Symplectic Mapping)

Let $g : U \to \mathbb{R}^{2dN}$ be a differentiable map, $U \subseteq \mathbb{R}^{2dN}$ open, then call the map g *symplectic*, if

$$\omega(\mathrm{D}g \cdot \eta, \mathrm{D}g \cdot \xi) = \omega(\eta, \xi)$$

holds for all η, ξ. Or equivalently $(\mathrm{D}g)^T \circ J \circ \mathrm{D}g = J$.

A numerical one step method is called symplectic if the numerical flow $\Phi_h : \mathcal{M} \to \mathcal{M}$ is a symplectic map.


Dg
η
ξ
(q, p)
g
Dg · ξ
g(q, p)
Dg · η

Theorem (Poincare 1899, [HLW06, Theorem VI.2.4])

Let $\mathcal{H}(\mathbf{q}, \mathbf{p})$ be a twice continuously differentiable function on $U \subset \mathbb{R}^{dN}$ open. Then, for each fixed time t, the flow φ_t is a symplectic transformation wherever it is defined.

Backward Analysis

Consider a general ODE $\dot{\mathbf{y}} = f(\mathbf{y})$.

Let $\mathbf{y}_n$ be the numerical solution, for a step size h then the modified equation is defined as

$$\begin{cases} \dot{\widetilde{\mathbf{y}}} & = f(\widetilde{\mathbf{y}}) + hf_2(\widetilde{\mathbf{y}}) + h^2 f_3(\widetilde{\mathbf{y}}) + \dots \\ \dot{\widetilde{\mathbf{y}}}(nh) & = \mathbf{y}_n \text{ for all } j = 0, 1, \dots. \end{cases}$$

We aim at finding the missing functions f_j to describe the numerical solutions as an exact solutions of the modified equation.

Backward Analysis

Lemma (Integrability Lemma, [HLW06] VI.2.7)

Let $D \subset \mathbb{R}^n$ be open and $f : D \to \mathbb{R}^n$ be continuously differentiable, and assume that the Jacobian $\mathrm{D}f(\mathbf{y})$ is symmetric for all $\mathbf{y} \in D$. Then, for every $\mathbf{y}_0 \in D$ there exists a neighbourhood and a function $H(\mathbf{y})$ such that

$$f(\mathbf{y}) = \nabla \mathcal{H}(\mathbf{y})$$

on this neighbourhood.

Backward Analysis

Theorem (Existence of a Local Modified Hamiltonian, [HLW06] Theorem IX.3.1)

If a symplectic method $\Phi_h(y)$ is applied to a Hamiltonian system with a smooth Hamiltonian $H : \mathbb{R}^{2n} \to \mathbb{R}$, the the modified equation is also Hamiltonian. More precisely, there exists smooth function $H_j : \mathbb{R}^{2n} \to \mathbb{R}$ for $j = 2, 3, \ldots,$ such that

$$f_j(\mathbf{y}) = J^{-1} \nabla H_j(\mathbf{y}).$$

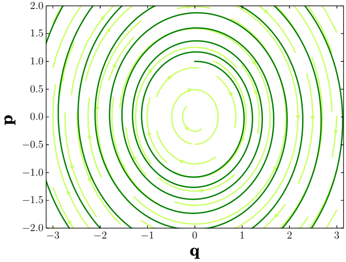
Basic Example: Harmonical Oscillator

For the Hamiltonian $\mathcal{H} = \frac{1}{2}p^2 + \frac{1}{2}q^2$, we get the system

$$\begin{cases} \dot{q} &= \dot{p}, \\ \dot{p} &= -\dot{q}. \end{cases}$$

Explicit Euler

Explicit Euler	**Symplectic Euler**
$p_{i+1} = p_i - hq_i$	$p_{i+1} = p_i - hq_i$
$q_{i+1} = q_i + hp_i$	$q_{i+1} = q_i + hp_{i+1}$



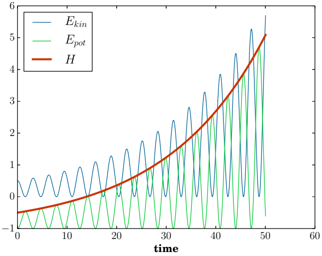
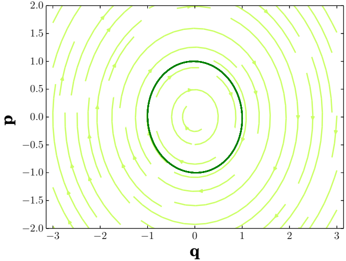


Figure: The explicit Euler method results in a dilation of the phase space. The energy increases.

Symplectic Euler

Explicit Euler	**Symplectic Euler**
$p_{i+1} = p_i - hq_i$	$p_{i+1} = p_i - hq_i$
$q_{i+1} = q_i + hp_i$	$q_{i+1} = q_i + hp_{i+1}$



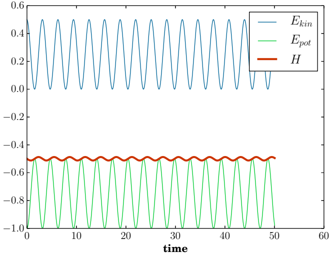
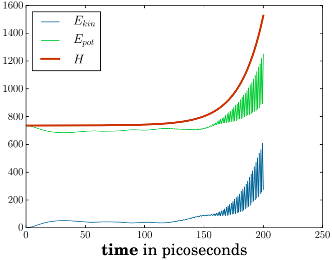


Figure: The symplectic Euler method has a better long time behaviour!

Conservation of Energy in the Application

Explicit Euler, $h = 10^{-2}$



Symplectic Euler, $h = 10^{-1}$

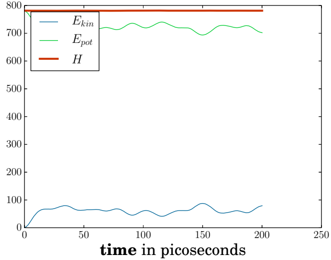


Figure: A step size of $h = 10^{-2}\,\mathrm{ns}$ leads to an explosion of the explicit euler approximation, whereas the symplectic method still remains stable with a larger step size of $h = 10^{-1}\,\mathrm{ns}$.

The Langevin Equation

For $\gamma \in (0,1)$, $m > 0$ and $\sigma \in \mathbb{R}^{dN \times dN}$, the Langevin equation is given by

$$\begin{aligned} \mathrm{d}\mathbf{Q} &= \nabla_P \mathcal{H}(\mathbf{Q}, \mathbf{P})\,\mathrm{d}t \\ \mathrm{d}\mathbf{P} &= -\nabla_Q \mathcal{H}(\mathbf{Q}, \mathbf{P})\,\mathrm{d}t - \gamma m \mathbf{P}\,\mathrm{d}t + \sigma\,\mathrm{d}\mathbf{W}_t. \end{aligned}$$

Theorem (Diffeomorphismtheorem, [KS12, Page 397])

Under usual assumptions (a, b globally Lipschitz and certain growth conditions) there exist a strong solution X of

$$\mathrm{d}X = a(X_t, t)\,\mathrm{d}t + b(X_t, t)\,\mathrm{d}W_t.$$

If additionally the coefficients a, b have bounded and continuous derivatices of all order up to $k \geq 1$, then there exist a version $\widetilde{X}$ of X such that for every $t \geq 0$ the map

$$\mathbf{x} \mapsto \widetilde{X}_t(\mathbf{x}, \omega)$$

is almost surely a $\mathcal{C}^{k-1}$ diffeomorphism.

Quiz:
When is the set of non-intersecting particle positions

$$\mathcal{M} = \{(\mathbf{q}_1, \dots, \mathbf{q}_N) \in (\mathbb{R}^d)^N \mid \mathbf{q}_i \in \mathbb{R}^d, \mathbf{q}_i \neq \mathbf{q}_j, \text{ for all } i \neq j\}$$

simply connected?

Thanks for your attention!

References I

- E. Hairer, C. Lubich, and G. Wanner, *Geometric numerical integration: Structure-preserving algorithms for ordinary differential equations*, Springer Series in Computational Mathematics, Springer Berlin Heidelberg, 2006.
- Ioannis Karatzas and Steven Shreve, *Brownian motion and stochastic calculus*, vol. 113, Springer Science & Business Media, 2012.