University at Buffalo
The State University of New York

Molecular Dynamics (adiabatic)

Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY 14260-3000

Alexey Akimov

"Excited States and Nonadiabatic Dynamics CyberTraining Workshop"
June 14, 2021

What is it?
Solving Newtonian equations of motion

$$\frac{dq_i}{dt} = v_i = \frac{p_i}{m_i},$$
$$\frac{dp_i}{dt} = F_i = -\frac{\partial U}{\partial q_i}.$$

Potential, depends on all coordinates in principle $\{q\}$

Definition!

If we recall

$$H = \sum_i \frac{p_i^2}{2m_i} + U(\{q\})$$

Hamiltonian dynamics!

Vectorized notation

Phase space coordinate representation

We realize

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i},$$
$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}.$$

$$\boldsymbol{q} = (q_0, q_1, \dots)^T$$
$$\boldsymbol{p} = (p_0, p_1, \dots)^T$$

$$\frac{d\boldsymbol{q}}{dt} = \frac{\partial H}{\partial \boldsymbol{p}},$$
$$\frac{d\boldsymbol{p}}{dt} = -\frac{\partial H}{\partial \boldsymbol{q}}.$$

$$\boldsymbol{z} = (\boldsymbol{q}, \boldsymbol{p})$$

$$\dot{\boldsymbol{z}} = \boldsymbol{J}\frac{dH}{d\boldsymbol{z}}$$

$$J = \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{I} \end{pmatrix}$$

Hamiltonian vs non-Hamiltonian dynamics

University at Buffalo
The State University of New York

Hamiltonian dynamics (e.g. isolated systems): there exists a function $H(\boldsymbol{q},\boldsymbol{p})$ $(\exists H)$ such that EOM are given by:

$$\frac{d\boldsymbol{q}}{dt} = \frac{\partial H}{\partial \boldsymbol{p}},$$
$$\frac{d\boldsymbol{p}}{dt} = -\frac{\partial H}{\partial \boldsymbol{q}}.$$

- The energy is conserved. The system's Hamiltonian is its energy
- The Hamiltonian yields EOMs

Non-Hamiltonian dynamics (e.g. open/dissipative systems): $\nexists H$ that would yield EOMs in Hamiltonian form

Example: add friction

$$\frac{d\boldsymbol{q}}{dt} = \frac{\partial H}{\partial \boldsymbol{p}},$$
$$\frac{d\boldsymbol{p}}{dt} = \boldsymbol{F} - \gamma\boldsymbol{p} = -\frac{\partial H}{\partial \boldsymbol{q}} - \gamma\boldsymbol{p}.$$

- The energy is not! conserved. There may exist conserved quantities, but they are not system's Hamiltonian
- The EOMs are not derived from the Hamiltonian via the $\dot{\boldsymbol{z}} = \boldsymbol{J}\frac{dH}{d\boldsymbol{z}}$ equation

Equations of motion

University at Buffalo
The State University of New York

Hamiltonian EOM
("Schrodinger" picture)
Evolve the system's state
CM: q and p; QM: wavefunction

Liouville's equation
("density matrix" picture)

$$\dot{\boldsymbol{q}} = \frac{d\boldsymbol{q}}{dt} = \frac{\partial H}{\partial \boldsymbol{p}},$$
$$\dot{\boldsymbol{p}} = \frac{d\boldsymbol{p}}{dt} = -\frac{\partial H}{\partial \boldsymbol{q}}.$$

$$\frac{d\rho(z)}{dt} = \{H, \rho\} + \frac{\partial \rho(z)}{\partial t} = iL\rho + \frac{\partial \rho(z)}{\partial t},$$

Classical Poisson bracket

$$\frac{d\rho(z)}{dt} = \sum_i \left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i \right) + \frac{\partial \rho(z)}{\partial t} = \sum_i \left(\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i} \right) + \frac{\partial \rho(z)}{\partial t} = \sum_i \left(\frac{\partial H}{\partial p_i}\frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial \rho}{\partial p_i} \right) + \frac{\partial \rho(z)}{\partial t} = iL\rho + \frac{\partial \rho(z)}{\partial t}$$

$$iL = \sum_i \left(\frac{\partial H}{\partial p_i}\frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial}{\partial p_i} \right)$$

Liouville's operator (Liouvillian)

Integrating equations of motion: Euler

University at Buffalo
The State University of New York

- Naïve approach: Euler, Verlet
- Predictor-corrector approaches
- Geometric integrators

$$\frac{dq(t)}{dt} \approx \frac{q(t+\Delta t) - q(t)}{\Delta t} = \frac{p(t)}{m} \Rightarrow q(t+\Delta t) = q(t) + \Delta t * \frac{p(t)}{m}$$

- same for momentum update
- need to coordinate timing

More accurately: $q(t+\Delta t) \approx q(t) + \frac{p(t)}{m}\Delta \mathrm{t} + \frac{1}{2!}\frac{\dot{p}(t)}{m}\Delta t^2 + \cdots$

Euler scheme

$$q_i(t+\Delta t) = q_i(t) + \Delta t * \frac{p_i(t)}{m_i}$$

$$p_i(t+\Delta t) = p_i(t) + \Delta t * f_i(t)$$

Algorithm

- Compute forces at $\boldsymbol{q}(t)$
- Update coordinates: $\boldsymbol{q} \rightarrow \boldsymbol{q} = \boldsymbol{q} + \Delta t \frac{\boldsymbol{p}}{\boldsymbol{m}}$
- Update momenta: $\boldsymbol{p} \rightarrow \boldsymbol{p} = \boldsymbol{p} + \Delta t\, \boldsymbol{f}$

Note: $f_i(t) = f\big(\boldsymbol{q}(t)\big)$ - the force is computed for the starting coordinates

Integrating equations of motion: (coordinate) Verlet/Leapfrog

University at Buffalo
The State University of New York

$$q(t+\Delta t) \approx q(t) + \dot{q}(t)\Delta \mathrm{t} + \frac{1}{2!}\ddot{q}(t)\Delta t^2 + \frac{1}{3!}\dddot{q}(t)\Delta t^3 + O(\Delta t^4) \ldots$$

$$q(t-\Delta t) \approx q(t) - \dot{q}(t)\Delta \mathrm{t} + \frac{1}{2!}\ddot{q}(t)\Delta t^2 - \frac{1}{3!}\dddot{q}(t)\Delta t^3 + O(\Delta t^4) \ldots$$

$$q(t+\Delta t) + q(t-\Delta t) = 2q(t) + \ddot{q}(t)\Delta t^2 + O(\Delta t^4) = 2q(t) + \frac{F(t)}{m}\Delta t^2 + O(\Delta t^4)$$

Leap-Frog

$$\boldsymbol{q(t+\Delta t) = 2q(t) - q(t-\Delta t) + 2\Delta t^2 \frac{F(t)}{m} + O(\Delta^4)}$$

Algorithm:

- Compute forces $\boldsymbol{F}$ at $\boldsymbol{q}(t)$
- Update coordinates: $\boldsymbol{q} \rightarrow \boldsymbol{q} = \boldsymbol{2q} - \boldsymbol{q}_{prev} + \Delta t \frac{\boldsymbol{F}}{\boldsymbol{m}}$
- Compute momenta using new and previous coordinates (for tracking)
- Swap variables: the former $\boldsymbol{q}$ becomes new $\boldsymbol{q}_{prev}$, ; the new $\boldsymbol{q}$ becomes the current $\boldsymbol{q}$

Exercises

- Implement Euler integration
- Implement the leap-frog integration
- Utilize the Runge-Kutta 4-th order integrator

Integrating equations of motion: Geometric integration (velocity Verlet)

University at Buffalo
The State University of New York

No explicit time-dependence $$\frac{d\rho(z(t))}{dt} = iL\rho(t) \Rightarrow \rho(t+\Delta t) = \exp(iL\Delta t)\,\rho(t)$$

What is this? $\exp(iL\Delta t)$

For 1D: $$iL = \left(\frac{\partial H}{\partial p}\frac{\partial}{\partial q} - \frac{\partial H}{\partial q}\frac{\partial}{\partial p}\right) = \left(\frac{p}{m}\frac{\partial}{\partial q} + F\frac{\partial}{\partial p}\right) = A + B$$

Trotter factorization: $\exp((A+B)\Delta t) \approx \exp\left(A\frac{\Delta t}{2}\right)\exp(B\Delta t)\exp\left(A\frac{\Delta t}{2}\right)$

$$\exp(iL\Delta t) \approx \exp\left(\frac{p\Delta t}{2m}\frac{\partial}{\partial q}\right)\exp\left(\Delta t F\frac{\partial}{\partial p}\right)\exp\left(\frac{p\Delta t}{2m}\frac{\partial}{\partial q}\right) = \exp\left(a\frac{\partial}{\partial q}\right)\exp\left(\mathrm{b}\frac{\partial}{\partial p}\right)\exp\left(a\frac{\partial}{\partial q}\right)$$

What do these operators do?

University at Buffalo
The State University of New York

$$\exp\left(a\frac{\partial}{\partial q}\right)\rho(q,p) = \left[1 + a\frac{\partial}{\partial q} + \frac{a^2}{2!}\frac{\partial^2}{\partial q^2} + \cdots\right]\rho(q,p) = \left[\rho(q,p) + a\frac{\partial\rho(q,p)}{\partial q} + \frac{a^2}{2!}\frac{\partial^2\rho(q,p)}{\partial q^2} + \cdots\right] \approx \rho(q+a,p)$$

So, it just advances q.

$$\exp\left(a\frac{\partial}{\partial q}\right): q \rightarrow q + a$$

Important: this is possible because a doesn't depend on q!

Likewise:

$$\exp\left(b\frac{\partial}{\partial p}\right): p \rightarrow p + b$$

Building an algorithm

University at Buffalo
The State University of New York

$$\rho(t+\Delta t) = \exp(iL\Delta t)\,\rho(t) \approx \exp\left(\frac{p\Delta t}{2m}\frac{\partial}{\partial q}\right)\exp\left(\Delta t F\frac{\partial}{\partial p}\right)\exp\left(\frac{p\Delta t}{2m}\frac{\partial}{\partial q}\right)\rho(t)$$

Operations:

$$q \rightarrow q + \frac{\Delta t}{2}\frac{p}{m}$$

$$p \rightarrow p + \Delta t F$$

$$q \rightarrow q + \frac{\Delta t}{2}\frac{p}{m}$$

With the explicit timing:

$$q(t) \rightarrow q\left(t+\frac{\Delta t}{2}\right) = q(t) + \Delta t\frac{p(t)}{2m}$$

$$p(t) \rightarrow p(t+\Delta t) = p(t) + \Delta t F\left(q\left(t+\frac{\Delta t}{2}\right)\right)$$

$$q\left(t+\frac{\Delta t}{2}\right) \rightarrow q(t+\Delta t) = q\left(t+\frac{\Delta t}{2}\right) + \Delta t\frac{p(t+\Delta t)}{2m}$$

Alternative (more common) factorization

University at Buffalo
The State University of New York

$$\rho(t+\Delta t) = \exp(iL\Delta t)\,\rho(t) \approx \exp\left(\frac{\Delta t}{2}F\frac{\partial}{\partial p}\right)\exp\left(\Delta t\frac{p}{m}\frac{\partial}{\partial q}\right)\exp\left(\frac{\Delta t}{2}F\frac{\partial}{\partial p}\right)\rho(t)$$

Operations:

$$p \to p + \frac{\Delta t}{2}F$$

$$q \to q + \Delta t\frac{p}{m}$$

$$p \to p + \frac{\Delta t}{2}F$$

With the explicit timing:

$$p(t) \to p\left(t+\frac{\Delta t}{2}\right) = p(t) + \frac{\Delta t}{2}F(t)$$

$$q(t) \to q(t+\Delta t) = q(t) + \Delta t\frac{p\left(t+\frac{\Delta t}{2}\right)}{m}$$

$$p\left(t+\frac{\Delta t}{2}\right) \to p(t+\Delta t) = p\left(t+\frac{\Delta t}{2}\right) + \frac{\Delta t}{2}F(t+\Delta t)$$