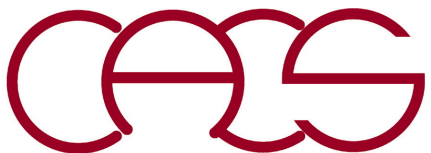


Molecular Dynamics Simulation: Q & A

Aiichiro Nakano

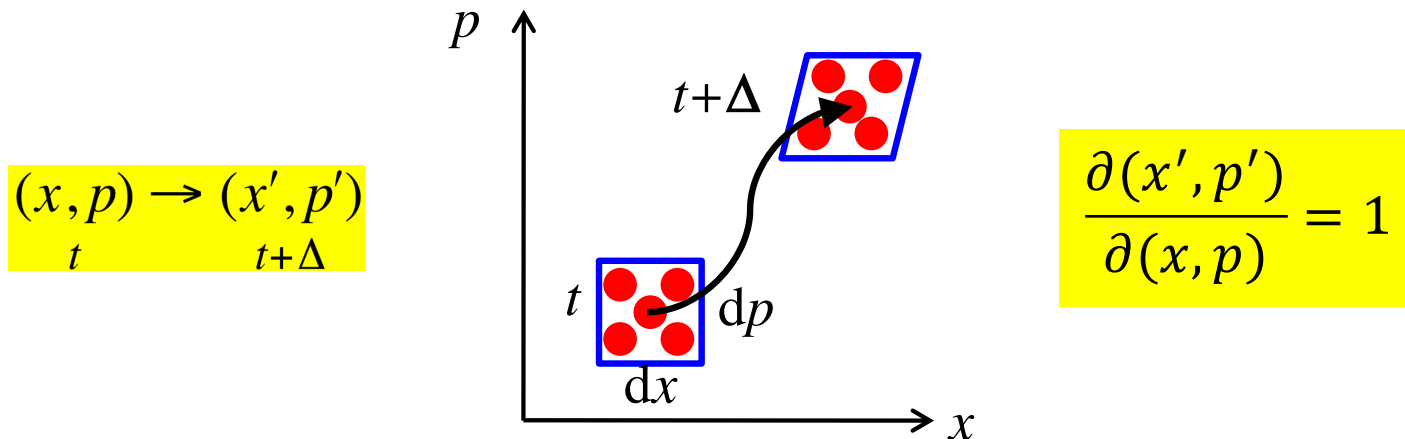
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Liouville's Theorem

Q: Why is it important to preserve the phase-space volume along the molecular-dynamics trajectory?



A: Exact phase-space-volume conservation tends to provide long-time stability, though formal analysis of long-time accuracy very hard.

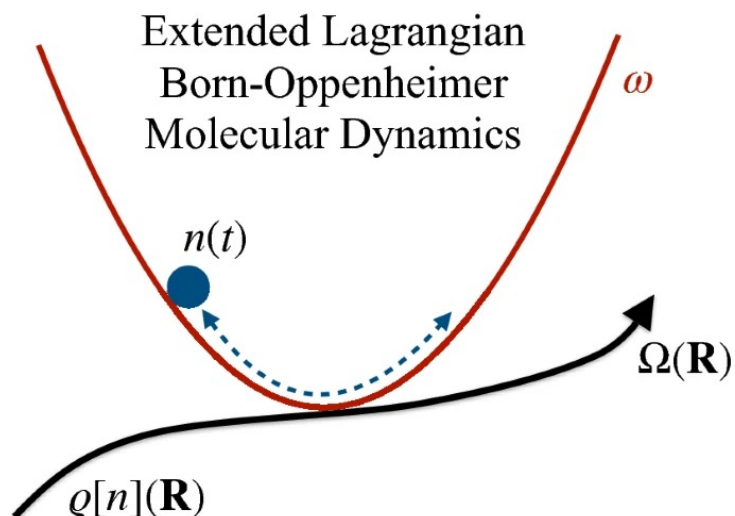
cf. Backward error analysis

S. Reich, *SIAM J. Numer. Anal.* **36**, 1549 ('99)

W. Hayes, *Appl. Num. Meth.* **53**, 299 ('05)

Shadow Molecular Dynamics

- **Extended-Lagrangian Born-Oppenheimer molecular dynamics (XL-BOMD), aka, shadow molecular dynamics:** Instead (of approximately solving the exact equations of motion), we calculate the exact electron density, energies, and forces, but for an underlying approximate shadow Born-Oppenheimer potential energy surface. In this way, the calculated forces are conservative with respect to the approximate shadow potential & generate accurate molecular trajectories with long-term energy stabilities.
- Shadow MD was inspired by backward error analysis.



A. M. N. Niklasson, *J. Chem. Phys.* **158**, 154105 ('23)

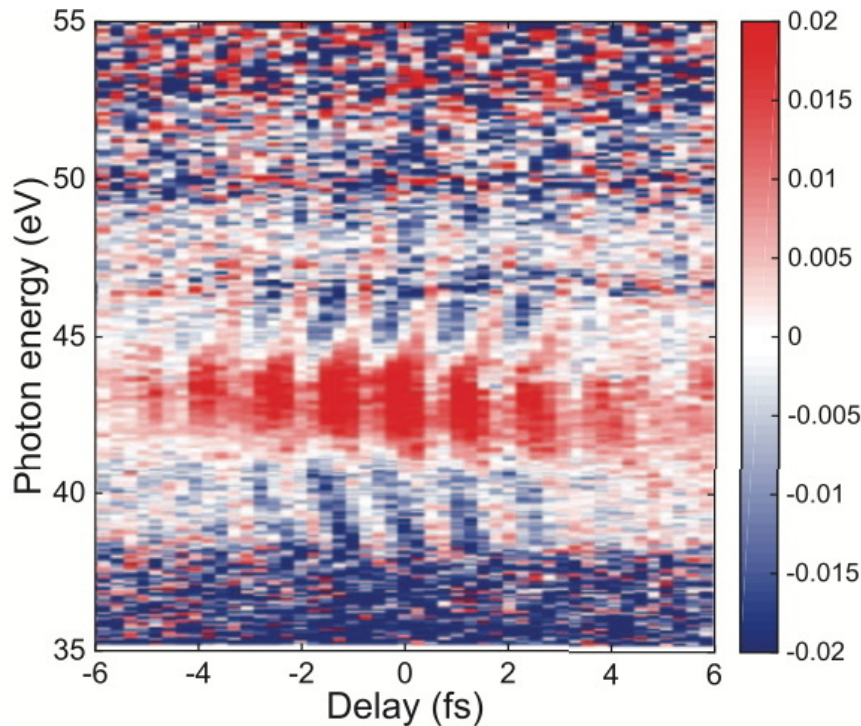
Velocity Autocorrelation (VAC)

Q: VAC in nonsteady state?

A: Present it as a function of two time variables.

$$\langle \vec{v}_i(t) \cdot \vec{v}_i(t') \rangle = vac \left(\tau = t - t', T = \frac{t + t'}{2} \right)$$

No T dependence in a steady state

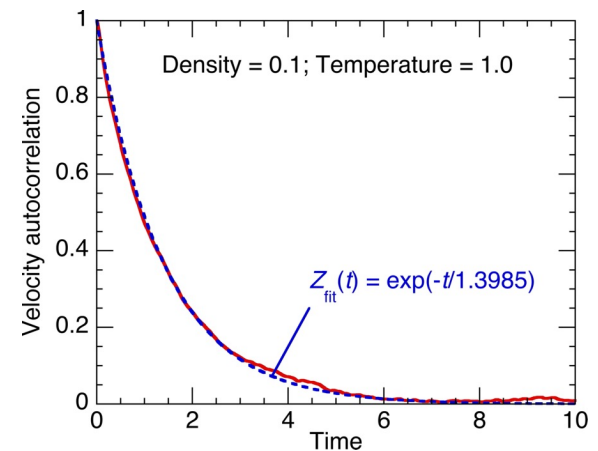
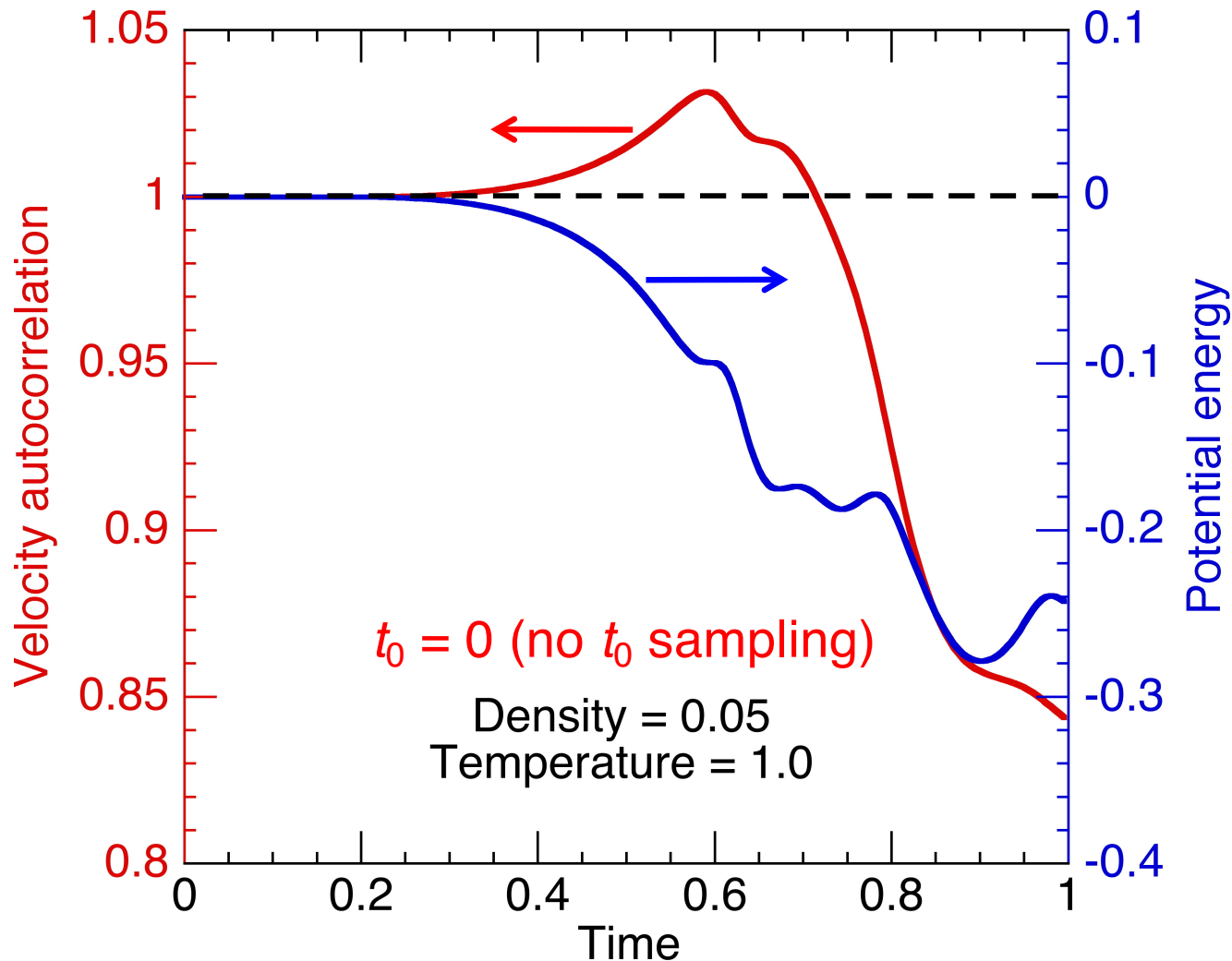


cf. Transient photoabsorption spectrum:
Note the atomic-unit energy, 27.2116 eV
= $h/(0.024 \text{ fs})$; h is Planck's constant

M. Lucchini *et al.*, *Science* **353**, 916 ('16)

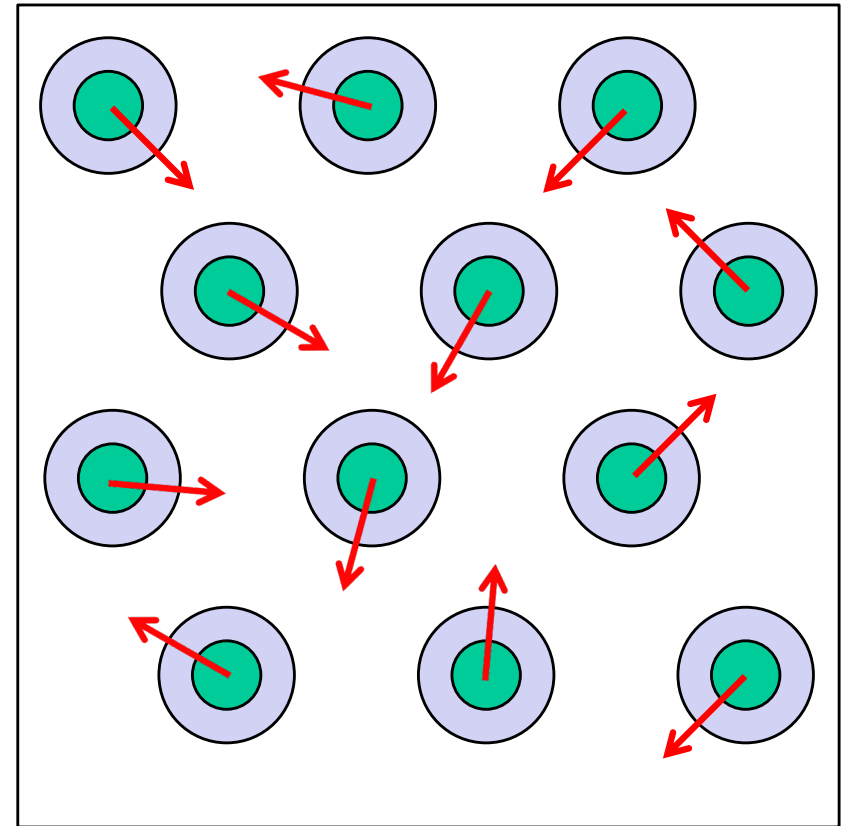
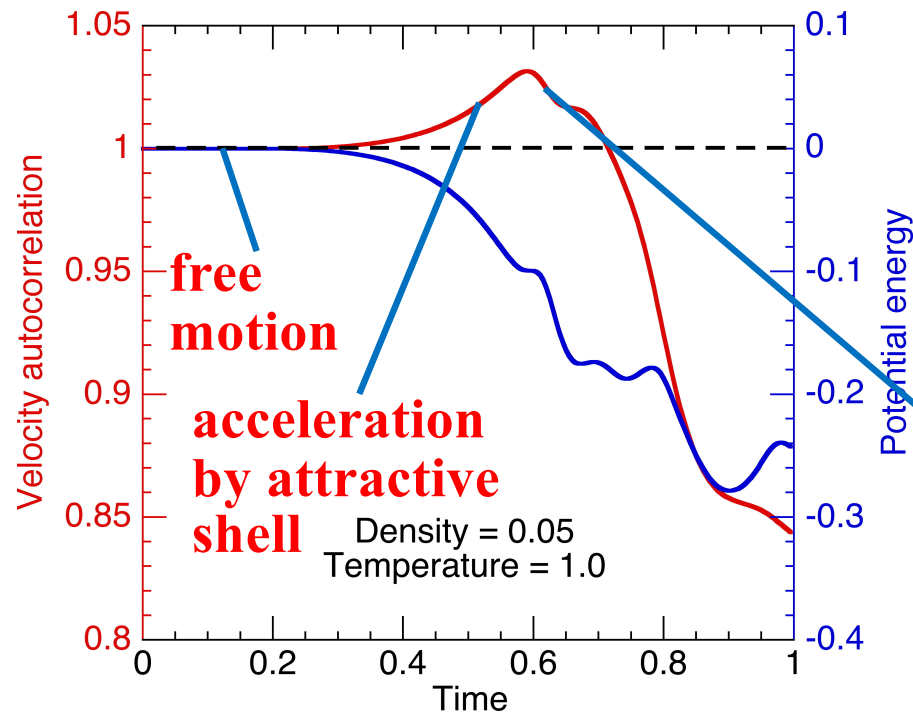
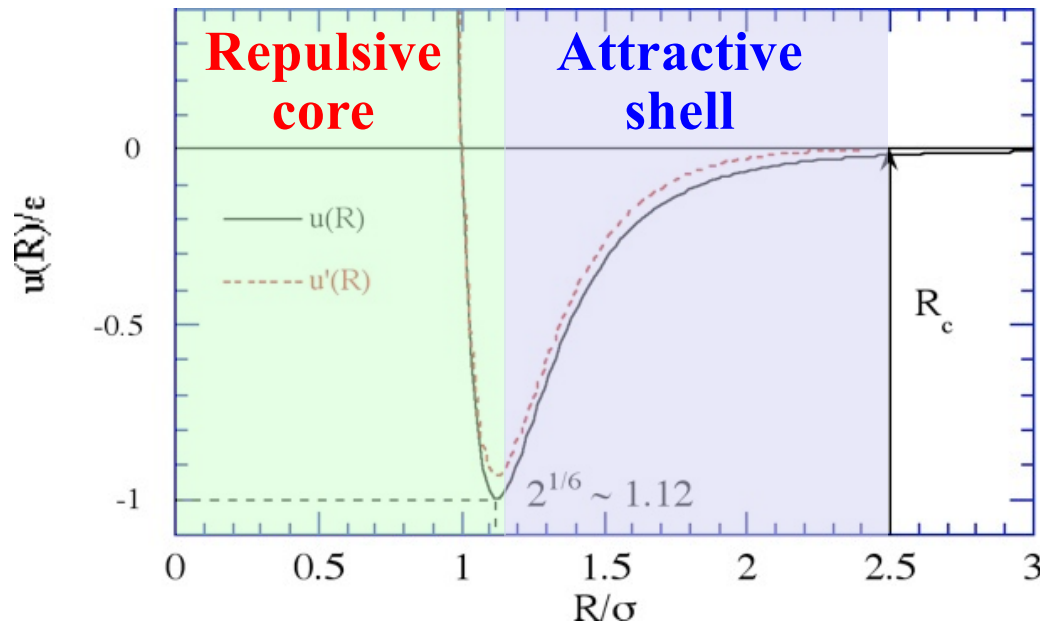
Velocity Autocorrelation > 1?

- Yes, in a gas phase just when starting from an FCC lattice



- Why? Hint = time variation of the potential energy

Finite-Range Lennard-Jones Potential



Why Taylor Expansion?

$$\frac{d}{dt} \Gamma = \hat{L} \Gamma$$

$$\Downarrow \exp(\hat{L}t) \equiv \sum_{n=0}^{\infty} \frac{1}{n!} (\hat{L}t)^n$$

$$\Gamma(t) = \exp(\hat{L}t) \Gamma(0)$$

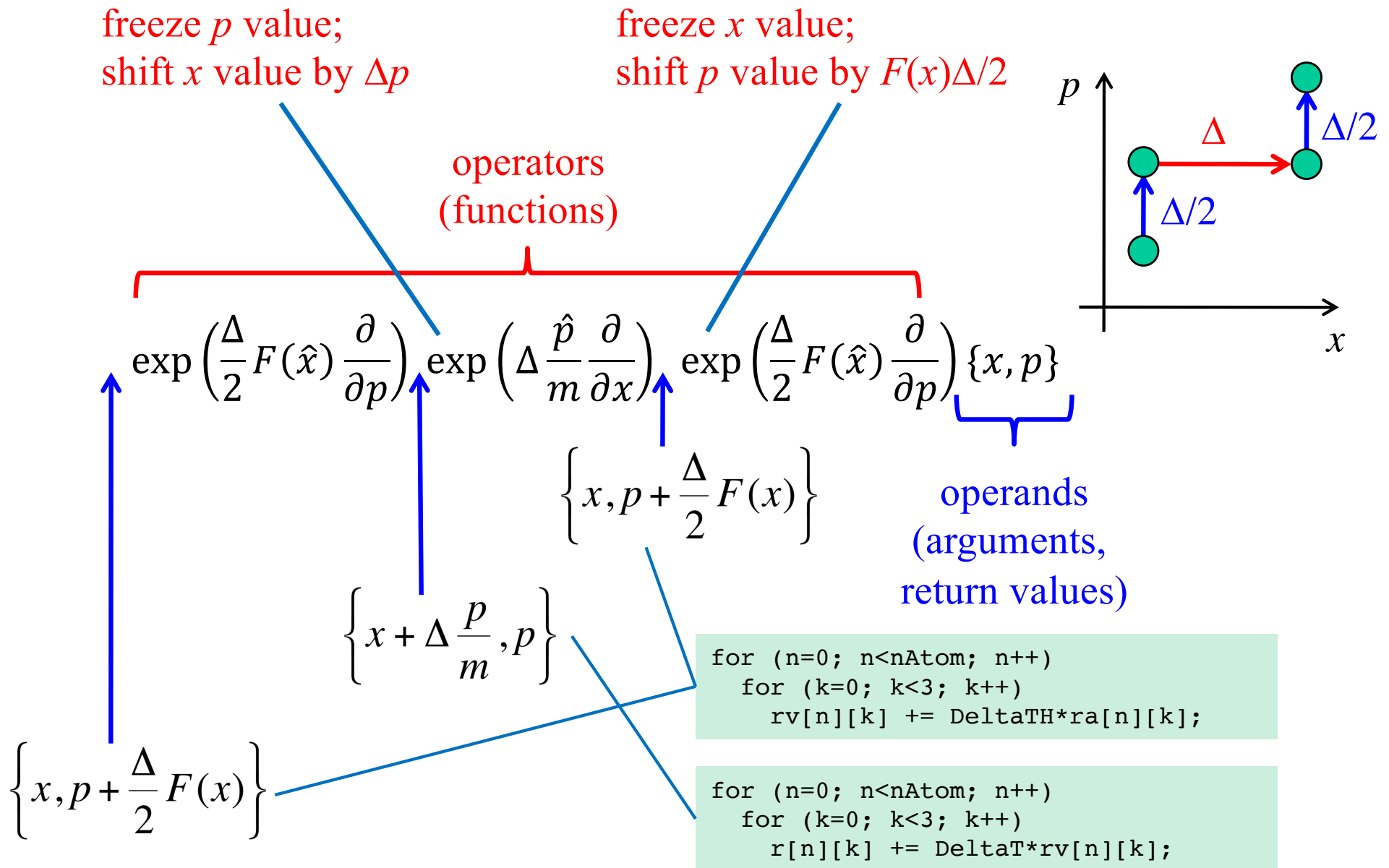
A: Exponentiation of a differential operator is “defined” through Taylor expansion, in which the power of the operator is operationally well defined as successive applications of the operator

$$\left(t \left(F(x) \frac{\partial}{\partial p} + \frac{p}{m} \frac{\partial}{\partial x} \right) \right)^3 f(x, p) =$$
$$t \left(F(x) \frac{\partial}{\partial p} + \frac{p}{m} \frac{\partial}{\partial x} \right) \left\{ t \left(F(x) \frac{\partial}{\partial p} + \frac{p}{m} \frac{\partial}{\partial x} \right) \left[t \left(F(x) \frac{\partial}{\partial p} + \frac{p}{m} \frac{\partial}{\partial x} \right) f(x, p) \right] \right\}$$

But it is very hard to obtain a closed form → do Trotter expansion

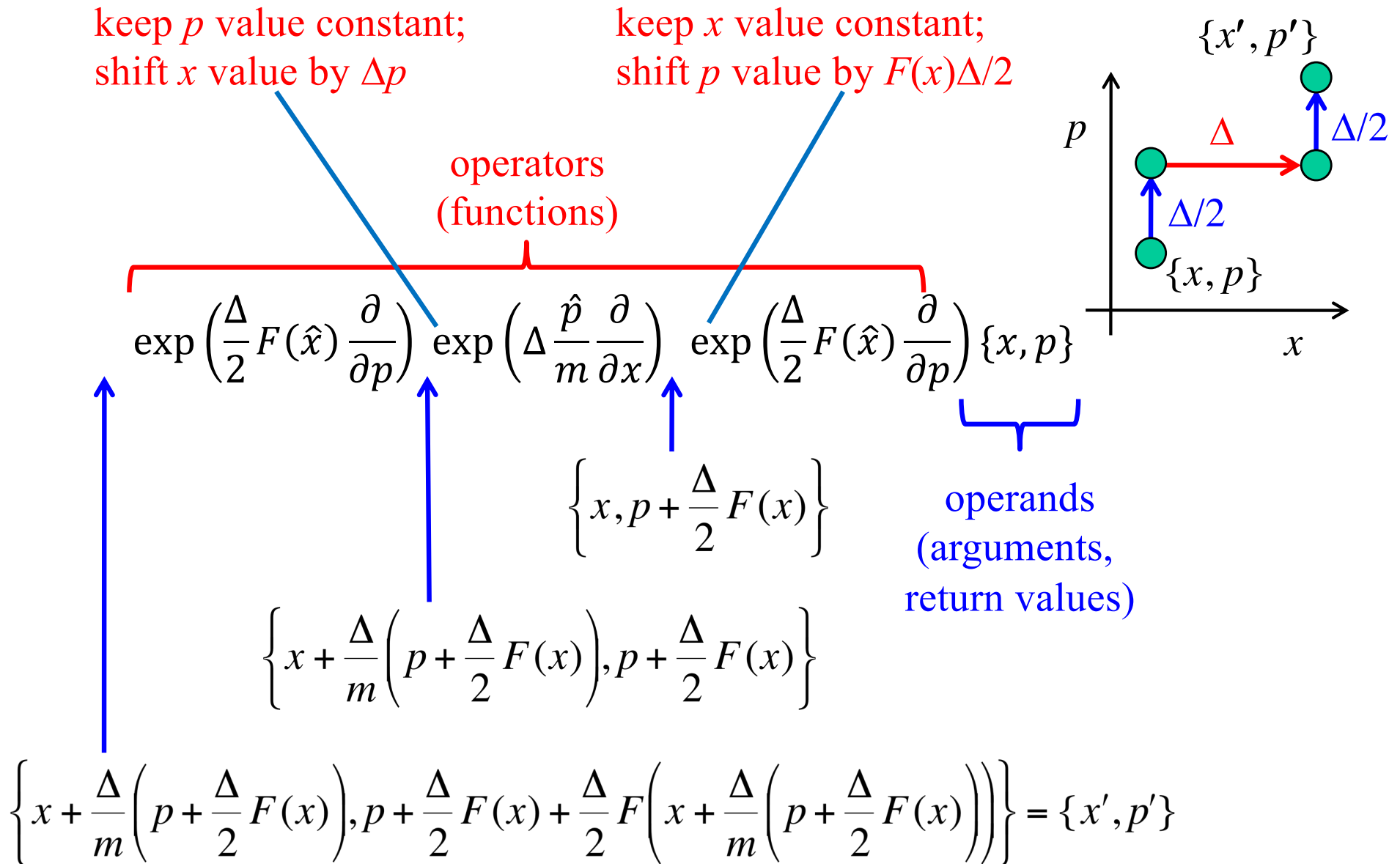
$$\{?, ?\} = \exp \left[t \left(F(x) \frac{\partial}{\partial p} + \frac{p}{m} \frac{\partial}{\partial x} \right) \right] \{x, p\}$$

Velocity Verlet Time Propagator?



It's shift operation!

Explicit Form of Mapping?



This is what we used in assignment 4, part 1!