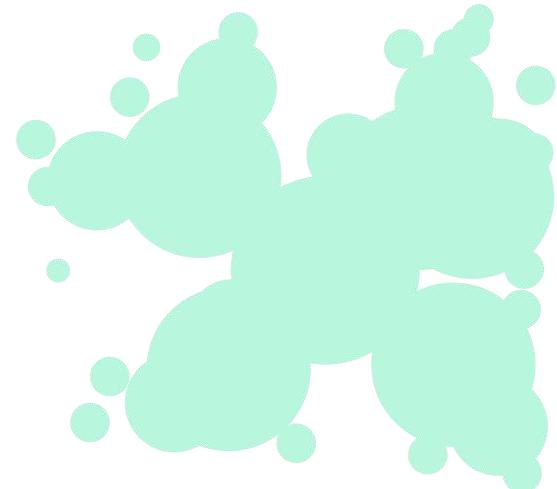


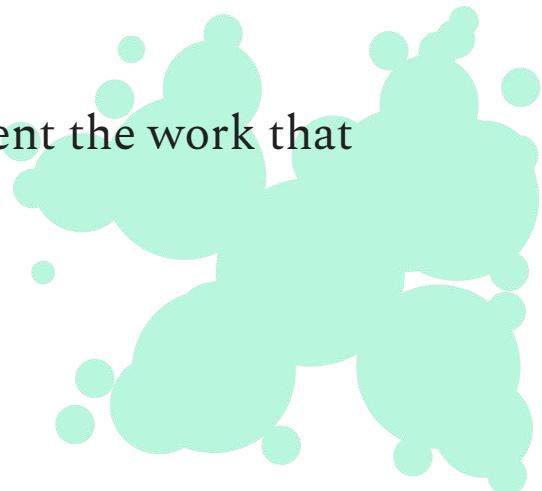
A new approach to finding the quantum ground state for atomic nuclei

Simone Sturniolo

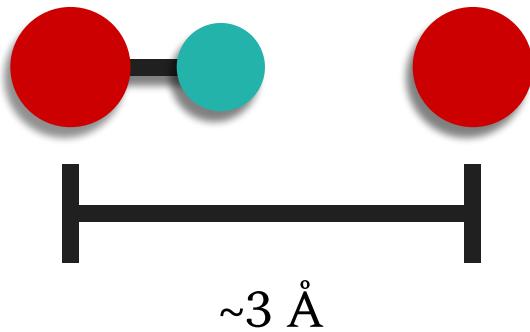


Timeline

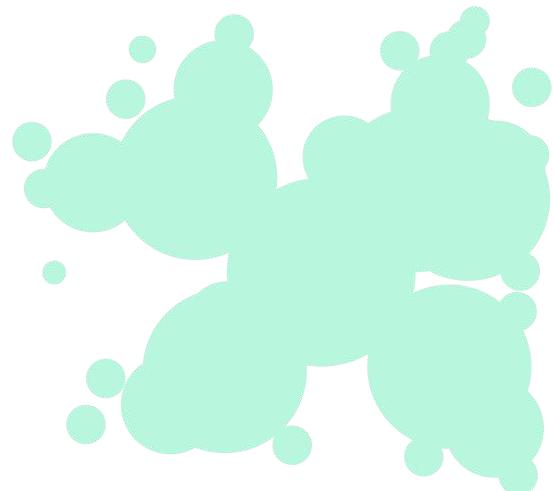
- 2014 - Original paper that inspired this project
- 2018 - My main paper on the subject
- 2019 - Attempt at getting funding from a Future Leaders Fellowship (failed)
- 2021 - Got some funding from the CSED Innovation and Development Programme
- 2022 - I will leave STFC in March, so I wanted to document the work that hasn't made it into a paper yet!



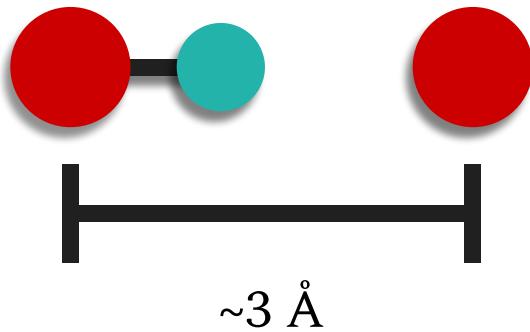
Why nuclear quantum effects?



$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$



Why nuclear quantum effects?



$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$

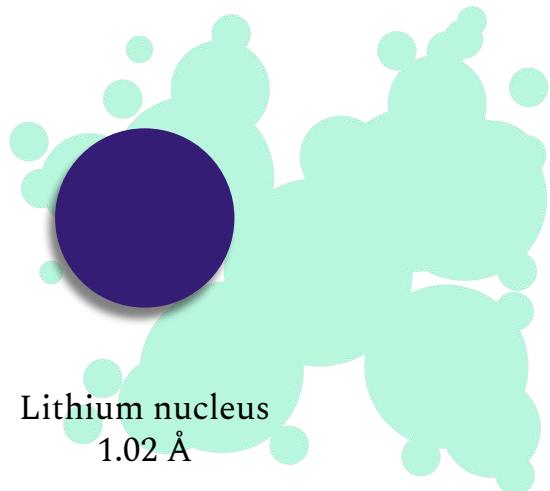
HO, $k \sim 0.35 \text{ eV}/\text{\AA}^2$



Electron
10.8 Å

Muon
2.86 Å

Hydrogen nucleus
1.66 Å



Lithium nucleus
1.02 Å

Why nuclear quantum effects?

T. E. Markland, M. Ceriotti, “Nuclear Quantum Effects enter the mainstream”, *Nature Reviews Chemistry* **2**, 0109 (2018)

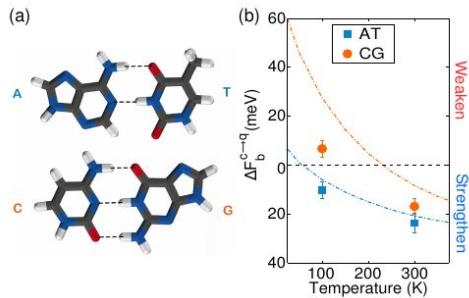


FIG. 2. (a) Structure of hydrogen-bonded base pair complexes of adenine-thymine (AT) and cytosine-guanine (CG). (b) The binding free energy change due to NQE^s as a function of temperature in the AT and CG base pairs obtained from PIMD simulations. Negative values correspond to NQE^s strengthening the hydrogen bonds between the base pairs and negative values correspond to weakening. The dashed lines show the harmonic predictions. *Adapted from Ref. [99]*

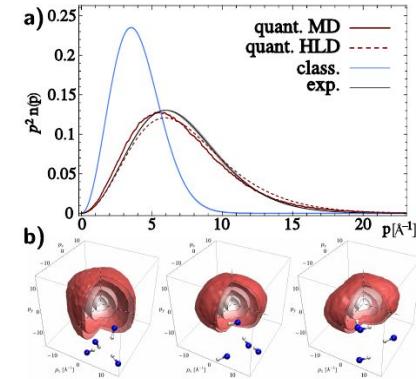


FIG. 4. (a) Particle-momentum distribution $p^2 n(p)$ for a Li_2NH polycrystalline sample, as measured by deep inelastic neutron scattering (black line), and as computed using a quantum thermostat (full red line). A Maxwell-Boltzmann distribution at the experimental temperature $T = 300\text{K}$ (blue line), and the curve computed for a Debye crystal based on the ab initio density of states (dashed red line) are also drawn for reference. (b) The three-dimensional PMD for three proposed crystal structures of Li_2NH ; that of Ref. [117] (left), that of Ref. [118] (center), and that of Ref. [119] (right) would make it possible to discriminate between the three proposals, that differ mostly by the orientation of the NH groups. *Adapted from Ref. [120]*

How to study nuclear quantum effects?

With experiments:

Directly with epi-thermal neutrons (VESUVIO instrument @ ISIS)

Indirectly through their effect on other measurable quantities like NMR parameters, IR absorption, chemical reaction rates

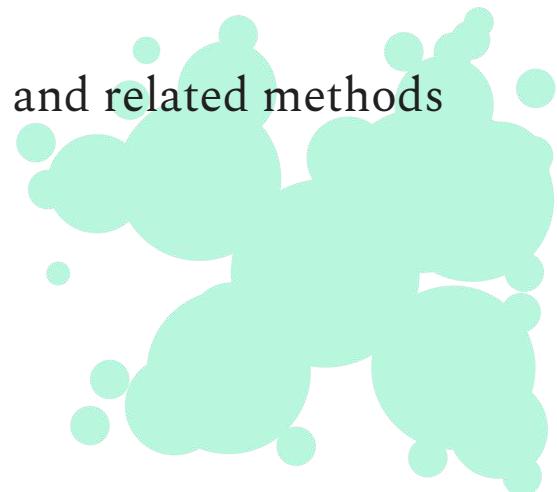


How to study nuclear quantum effects?

With simulations:

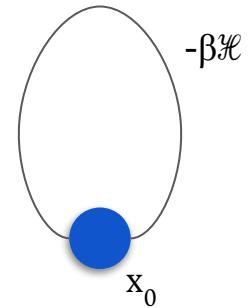
Nuclear-Electronic Orbital multi component DFT (NEO-DFT)

Path Integral Molecular Dynamics, Ring Polymer Dynamics, and related methods



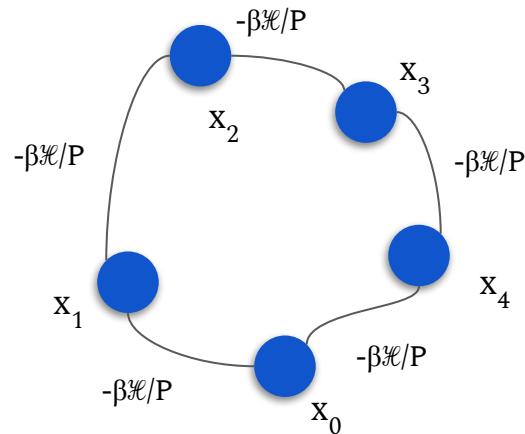
Path Integral Molecular Dynamics

$$P(x_0) = \langle x_0 | e^{-\beta \frac{\mathcal{H}}{\hbar}} | x_0 \rangle$$

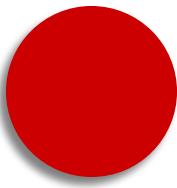


Path Integral Molecular Dynamics

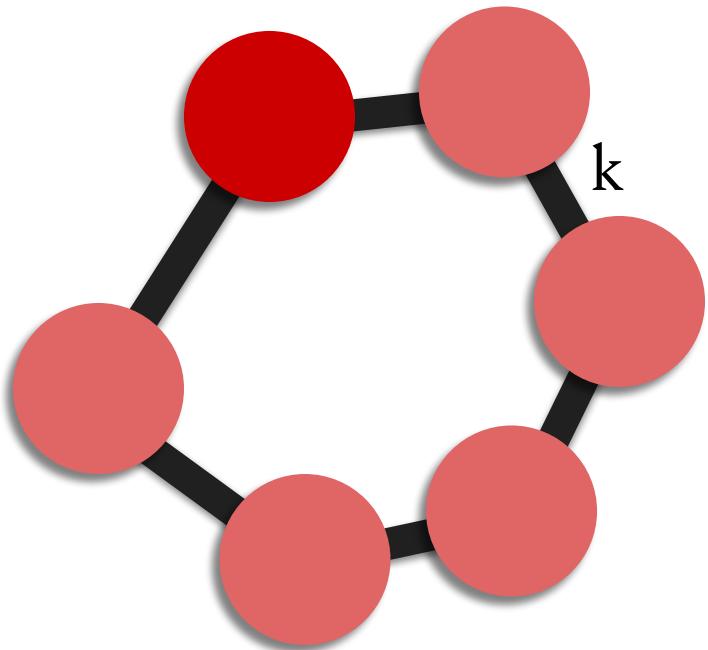
$$P(x_0) = \langle x_0 | e^{-\beta \frac{\mathcal{H}}{\hbar P}} | x_1 \rangle \dots \langle x_n | e^{-\beta \frac{\mathcal{H}}{\hbar P}} | x_0 \rangle$$



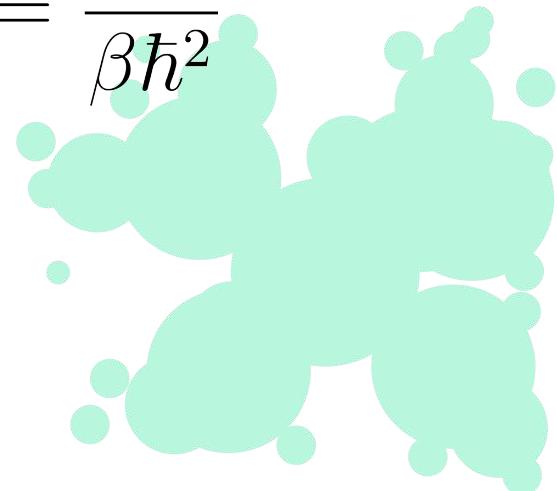
Path Integral Molecular Dynamics



Path Integral Molecular Dynamics



$$k = \frac{mP}{\beta \hbar^2}$$

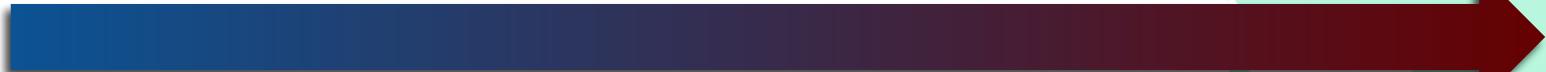


Path Integral Molecular Dynamics

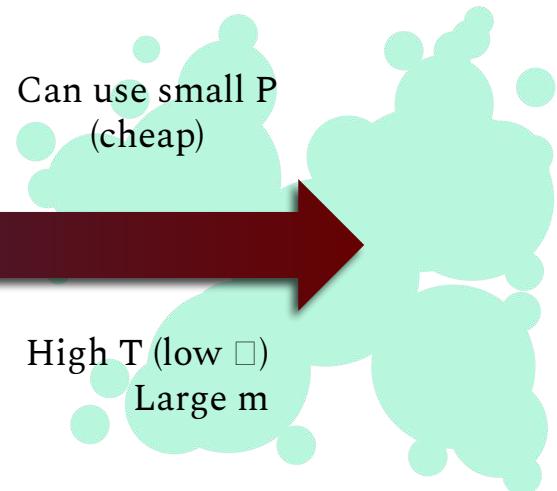
- Focuses on thermal density matrix (mixed state)
- The “dynamics” are not real time, and actually just sample the space of paths
- Additional steps needed for time correlations or momenta distributions

$$k = \frac{mP}{\beta\hbar^2}$$

Must use large
P (expensive)



Low T (high \square)
Small m

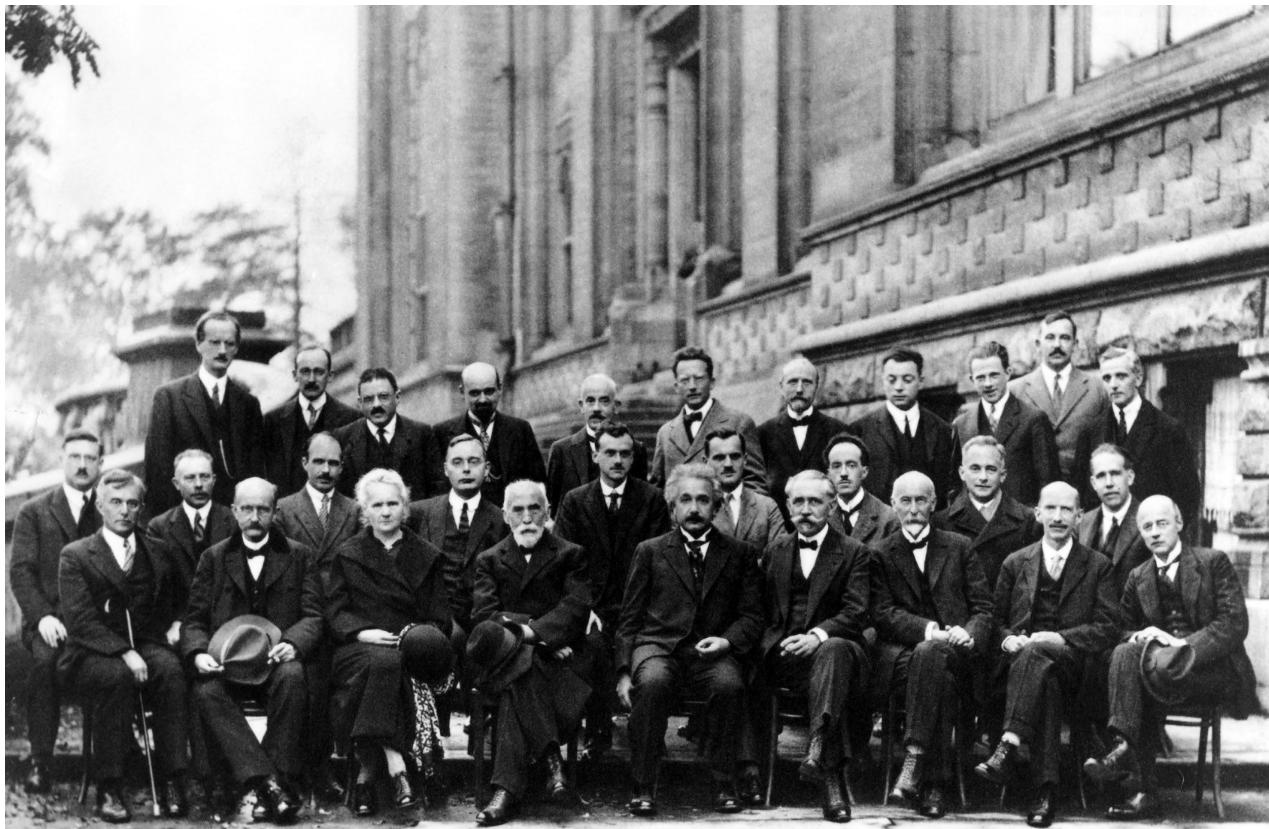


High T (low \square)
Large m

$$k = \frac{mP}{\beta\hbar^2}$$

Is there another way?





Source: Wikimedia Commons

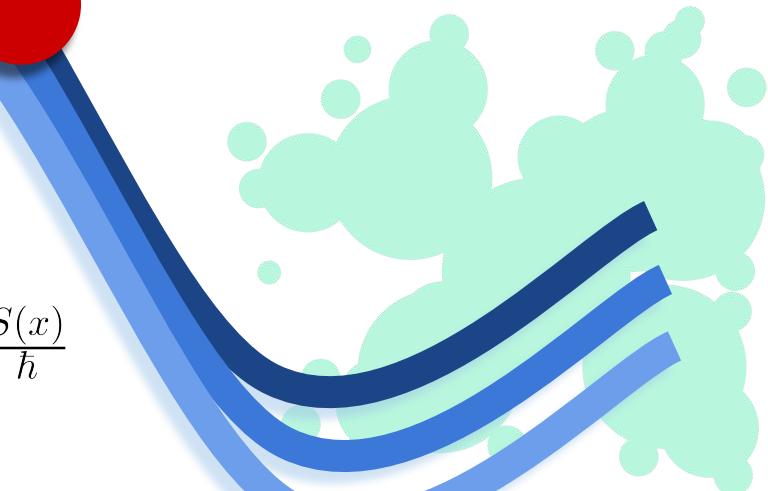
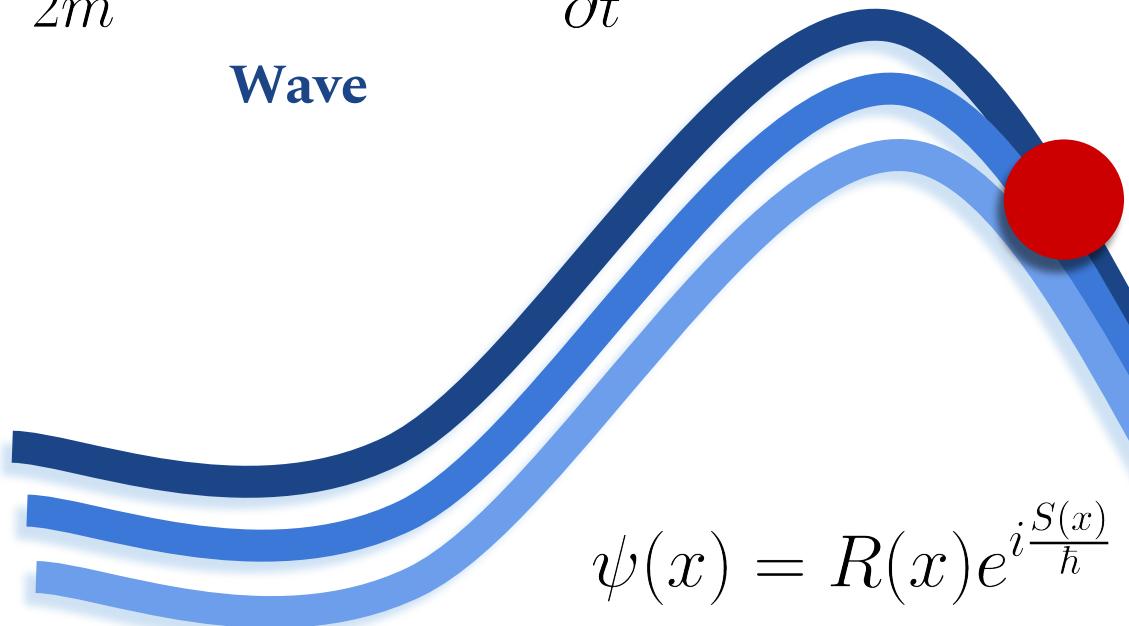
The De Broglie - Bohm pilot wave interpretation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = i\hbar \frac{\partial \psi}{\partial t}$$

Wave

$$\vec{v} = \frac{\nabla S}{m}$$

Particle



The De Broglie - Bohm pilot wave interpretation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t}$$

Wave

$$\vec{v} = \frac{\nabla S}{m}$$

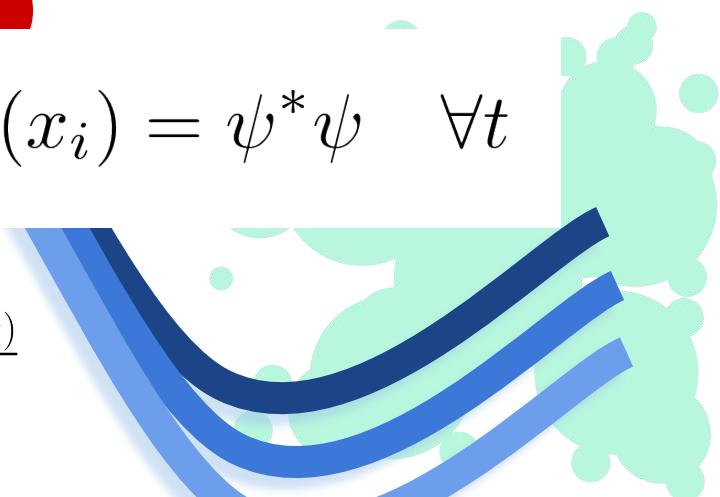


Particle

$$P(x_i) = \psi^*\psi \quad t = 0 \implies P(x_i) = \psi^*\psi \quad \forall t$$



$$\psi(x) = R(x)e^{i\frac{S(x)}{\hbar}}$$



The De Broglie - Bohm pilot wave interpretation

1952

**David
Bohm**



Source: Wikimedia
Commons

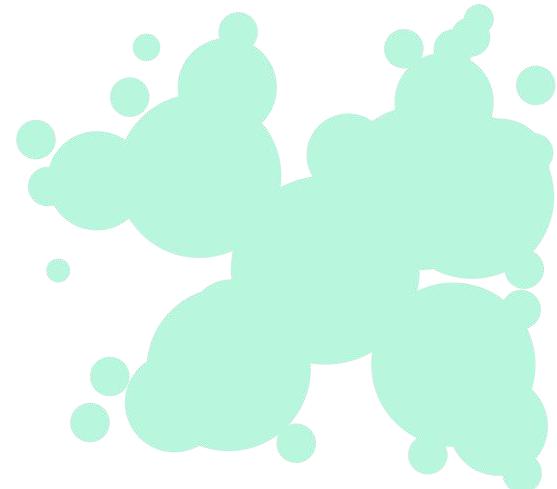


The De Broglie - Bohm pilot wave interpretation

$$\nabla^2\psi = \left[\frac{\nabla^2 R}{R} - \frac{(\nabla S)^2}{\hbar^2} + i \left(2\frac{1}{\hbar} \frac{\nabla R \nabla S}{R} + \frac{1}{\hbar} \nabla^2 S \right) \right] \psi$$

$$\frac{\partial\psi}{\partial t} = \left(\frac{1}{R} \frac{\partial R}{\partial t} + \frac{i}{\hbar} \frac{\partial S}{\partial t} \right) \psi$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = i\hbar \frac{\partial\psi}{\partial t}$$



David Bohm, A Suggested Interpretation of the Quantum Theory in Terms of “Hidden” Variables, Phys. Rev. 85 (1952)

The De Broglie - Bohm pilot wave interpretation

$$\nabla^2\psi = \left[\frac{\nabla^2 R}{R} - \frac{(\nabla S)^2}{\hbar^2} + i \left(2\frac{1}{\hbar}\frac{\nabla R \nabla S}{R} + \frac{1}{\hbar}\nabla^2 S \right) \right] \psi$$

$$\frac{\partial\psi}{\partial t} = \left(\frac{1}{R} \frac{\partial R}{\partial t} + \frac{i}{\hbar} \frac{\partial S}{\partial t} \right) \psi$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = i\hbar \frac{\partial\psi}{\partial t}$$

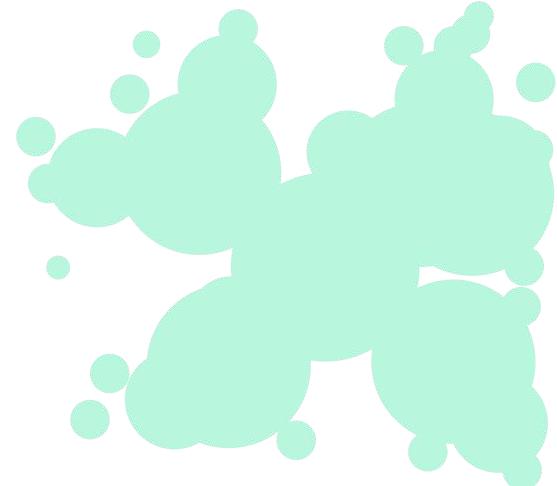


David Bohm, A Suggested Interpretation of the Quantum Theory in Terms of "Hidden" Variables, Phys. Rev. 85 (1952)

The De Broglie - Bohm pilot wave interpretation

$$\nabla^2 \psi = \left[\frac{\nabla^2 R}{R} - \frac{(\nabla S)^2}{\hbar^2} + i \left(2 \frac{1}{\hbar} \frac{\nabla R \nabla S}{R} + \frac{1}{\hbar} \nabla^2 S \right) \right] \psi$$

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= \left(\frac{1}{R} \frac{\partial R}{\partial t} + \frac{i}{\hbar} \frac{\partial S}{\partial t} \right) \psi \\ -\frac{\hbar^2}{2m} \frac{\nabla^2 R}{R} + \frac{(\nabla S)^2}{2m} + V &= -\frac{\partial S}{\partial t} \end{aligned}$$



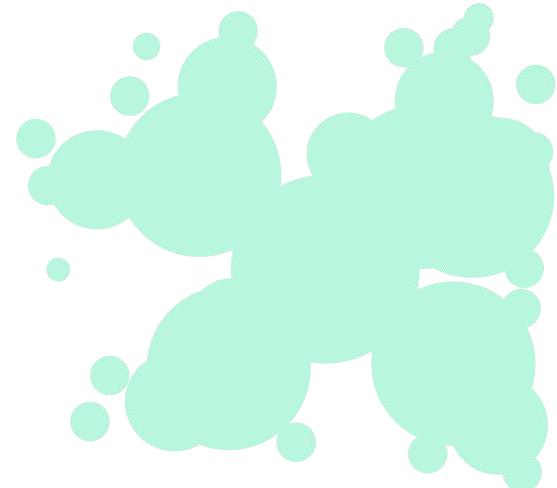
David Bohm, A Suggested Interpretation of the Quantum Theory in Terms of "Hidden" Variables, Phys. Rev. 85 (1952)

The De Broglie - Bohm pilot wave interpretation

Hamilton-Jacobi equation

$$H = -\frac{dS}{dt}$$

$$-\frac{\hbar^2}{2m} \frac{\nabla^2 R}{R} + \frac{(\nabla S)^2}{2m} + V = -\frac{\partial S}{\partial t}$$



David Bohm, A Suggested Interpretation of the Quantum Theory in Terms of "Hidden" Variables, Phys. Rev. 85 (1952)

The De Broglie - Bohm pilot wave interpretation

Hamilton-Jacobi equation

$$H = -\frac{dS}{dt}$$

Quantum potential

$$-\frac{\hbar^2}{2m} \frac{\nabla^2 R}{R} + \frac{(\nabla S)^2}{2m} + V = -\frac{\partial S}{\partial t}$$



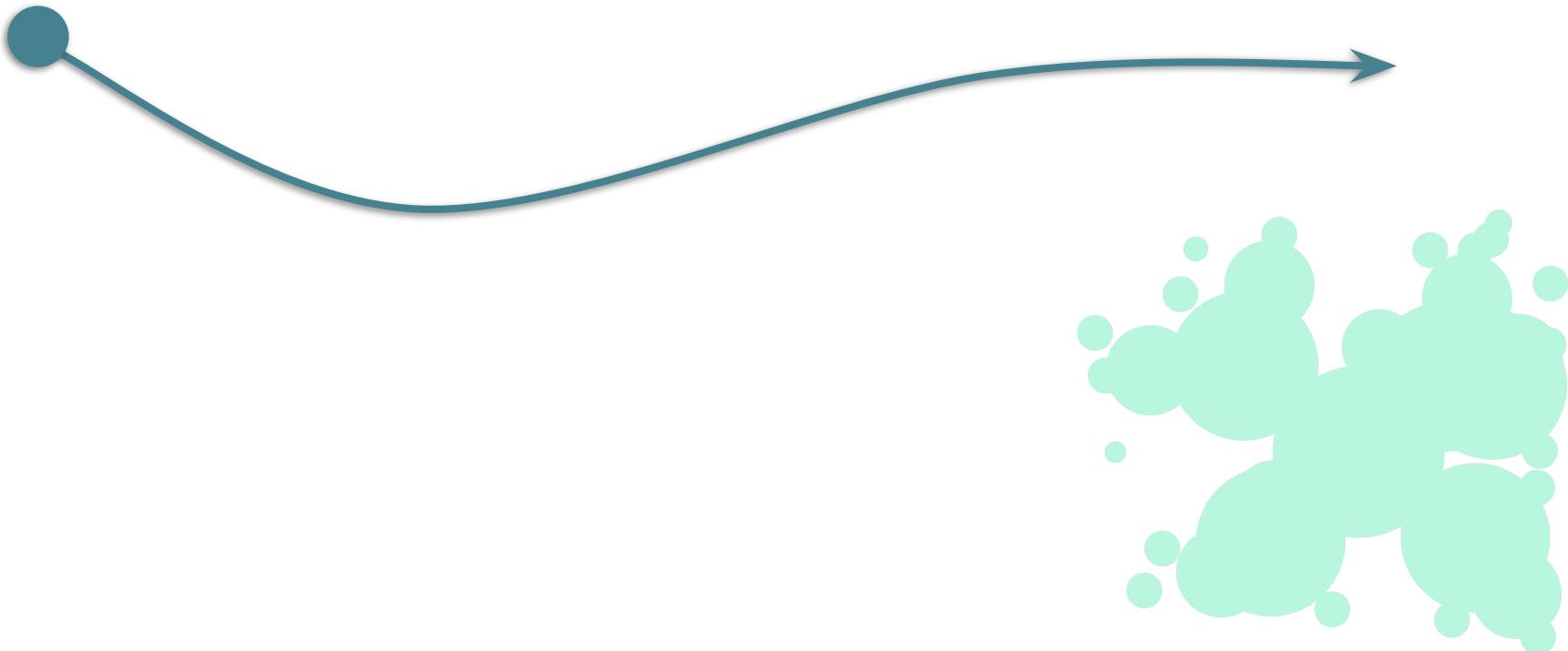
David Bohm, A Suggested Interpretation of the Quantum Theory in Terms of “Hidden” Variables, Phys. Rev. 85 (1952)

The Many Interacting Worlds interpretation

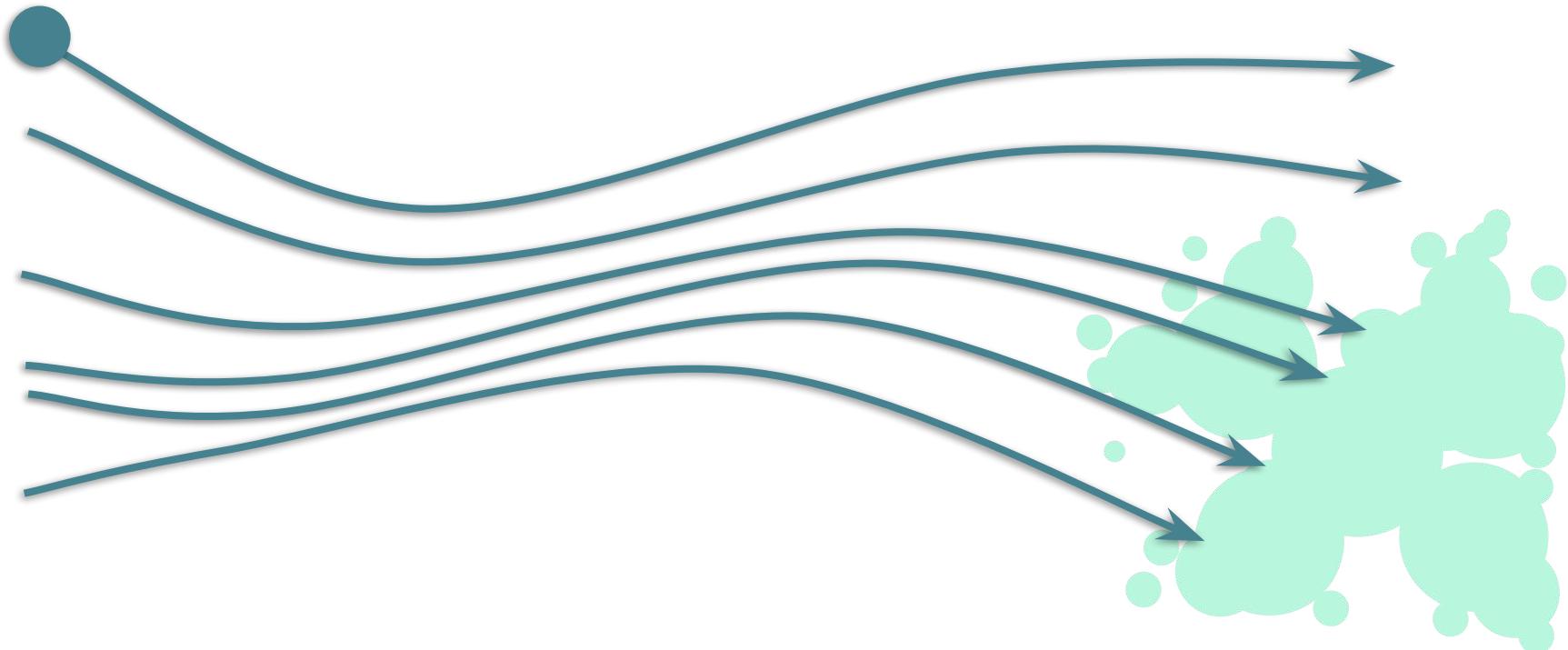
Michael J.W. Hall, Dirk-André Deckert, and Howard M. Wiseman,
**Quantum Phenomena Modeled by Interactions between Many
Classical Worlds, *Phys. Rev. X* 4 (2014)**



The Many Interacting Worlds interpretation

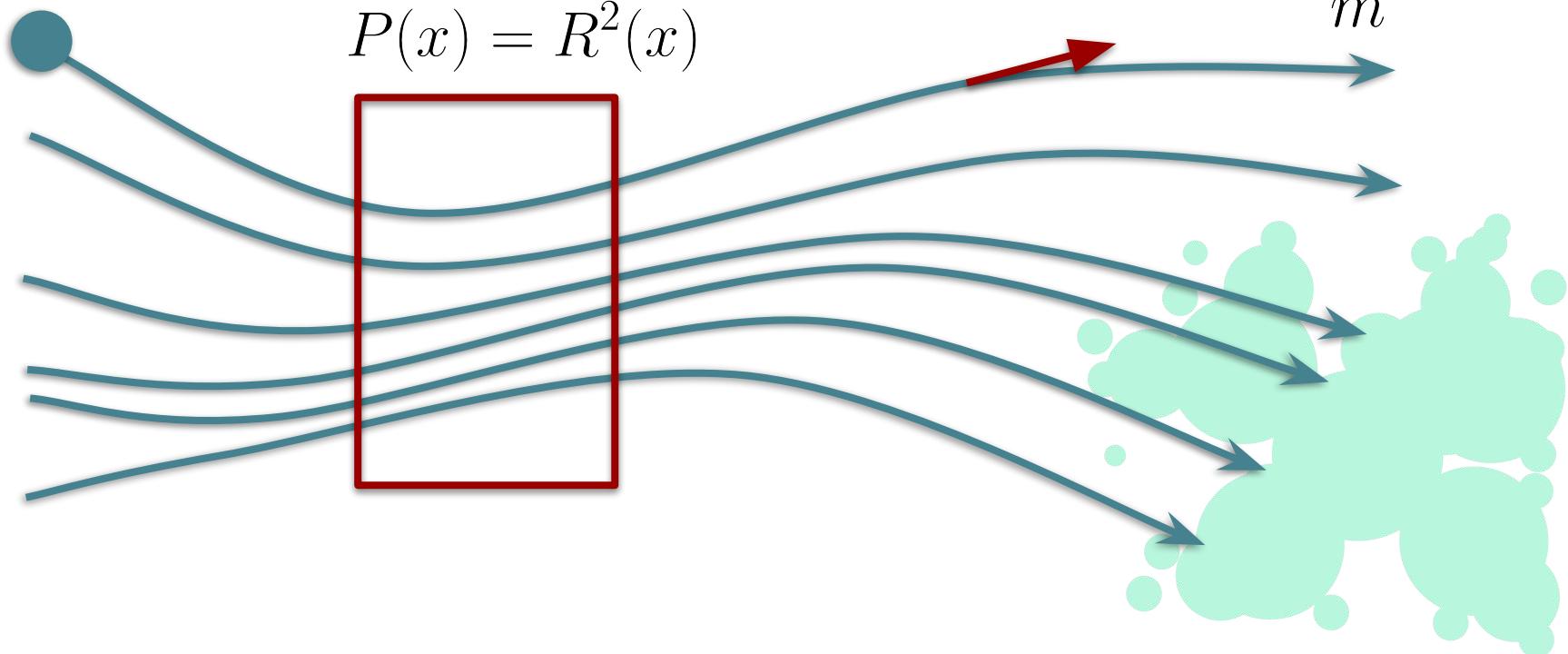


The Many Interacting Worlds interpretation



The Many Interacting Worlds interpretation

$$\vec{v}(x) = \frac{\nabla S(x)}{m}$$



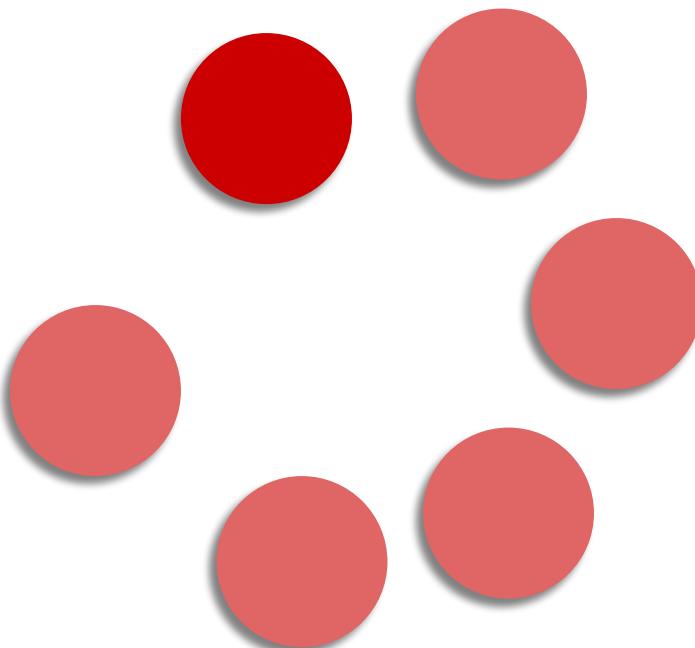
The Many Interacting Worlds interpretation

$$\begin{aligned}\langle V_Q \rangle &= \int_{-\infty}^{\infty} PV_Q dx = -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} R \nabla^2 R dx = \\ &\quad -\frac{\hbar^2}{2m} \left[R \nabla R \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} (\nabla R)^2 dx \right]\end{aligned}$$

$$\frac{\langle V_Q \rangle}{P} = \frac{\hbar^2}{2m} \frac{(\nabla R)^2}{R^2} = \frac{\hbar^2}{8m} \left(\frac{\nabla P}{P} \right)^2$$



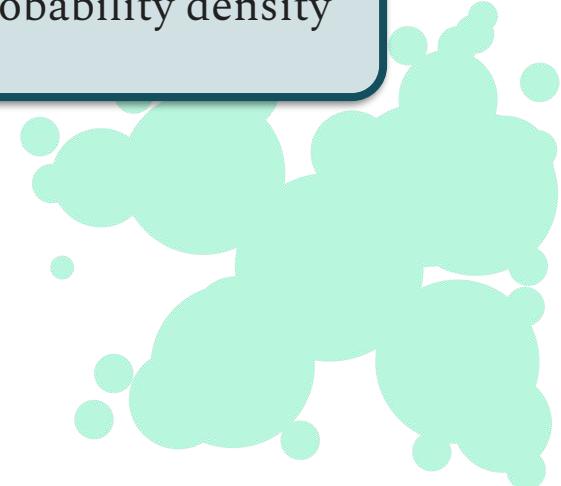
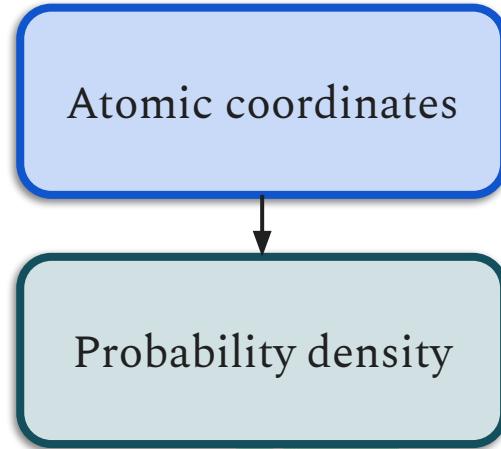
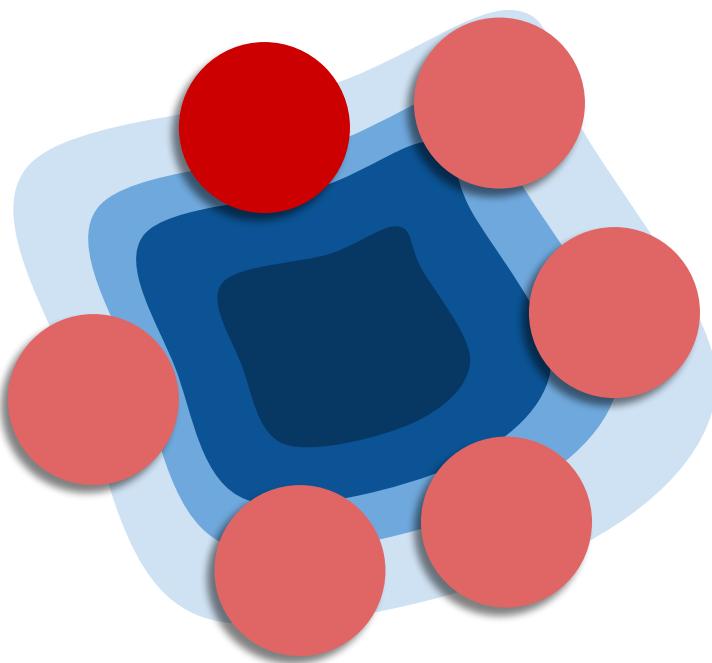
MIW Molecular Dynamics



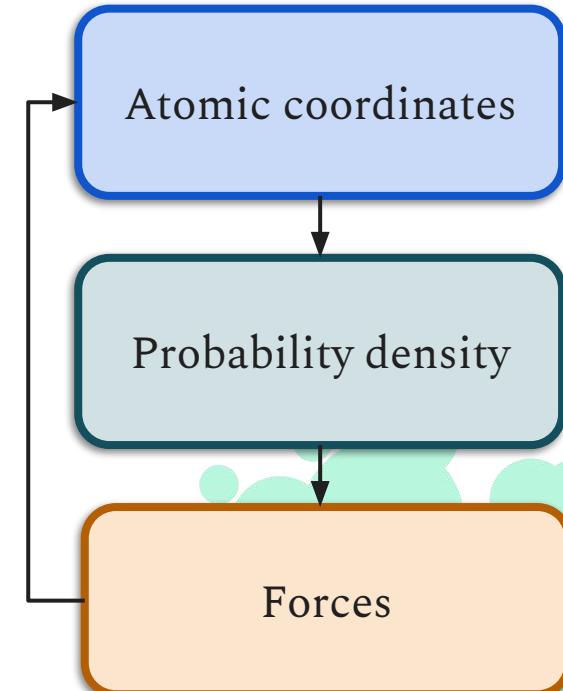
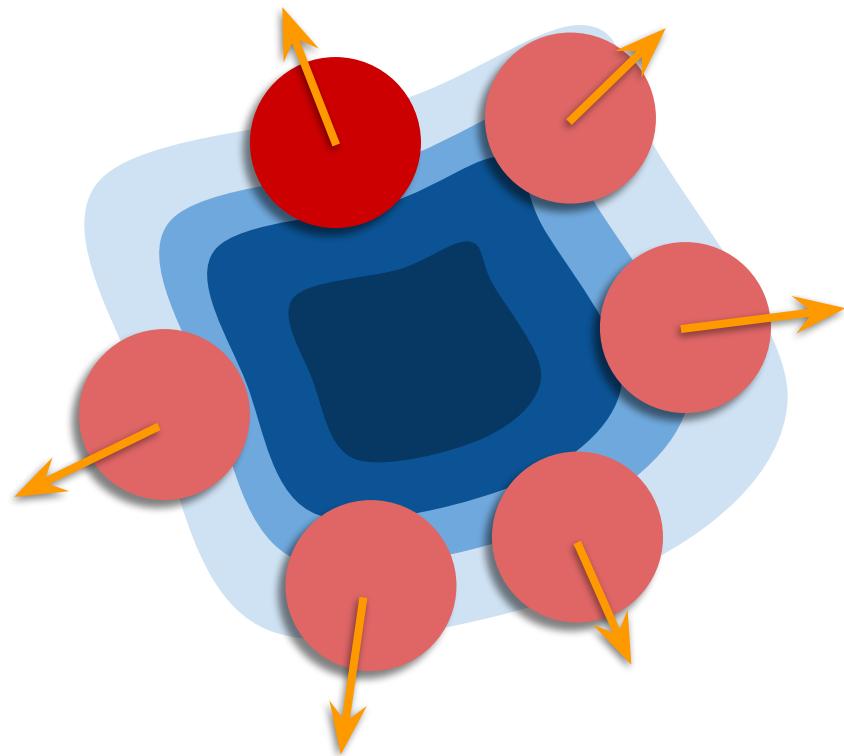
Atomic coordinates



MIW Molecular Dynamics



MIW Molecular Dynamics

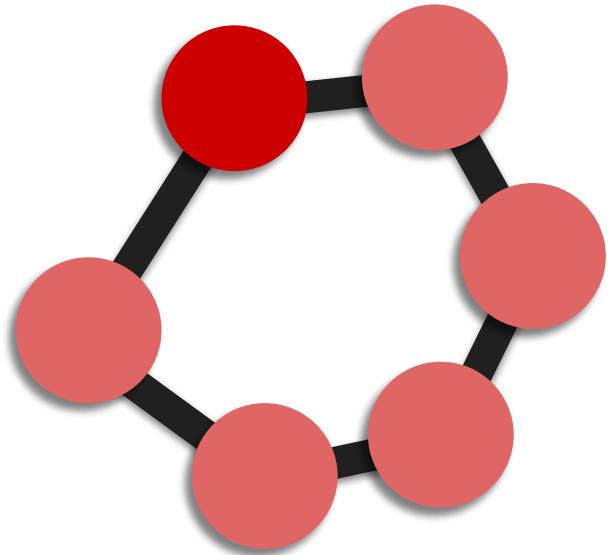


Atomic coordinates

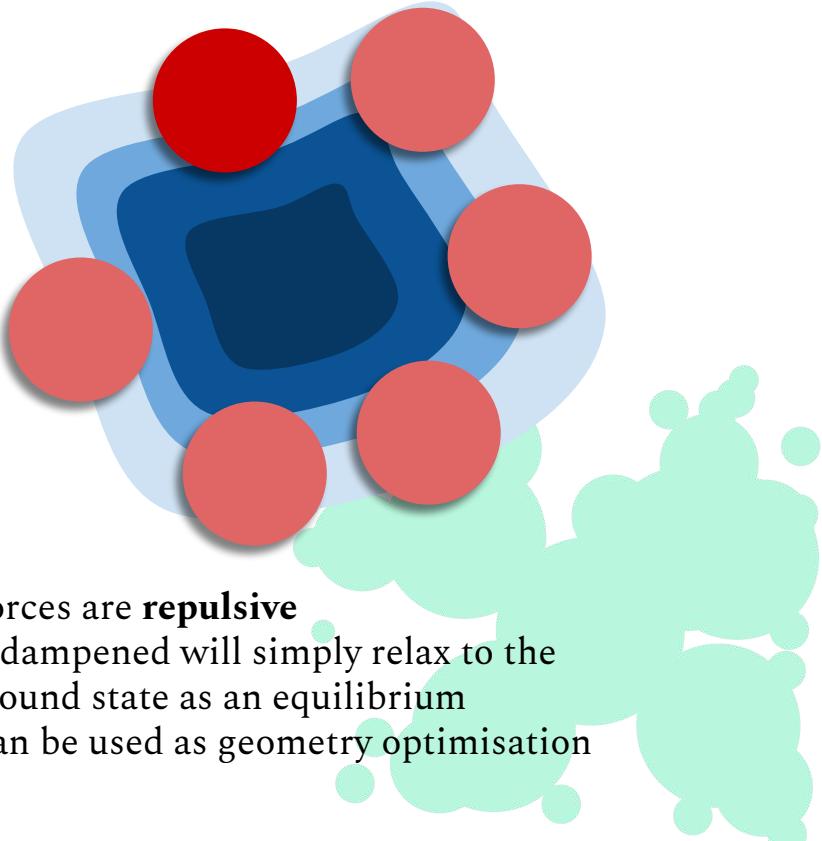
Probability density

Forces

PIMD v. MIW

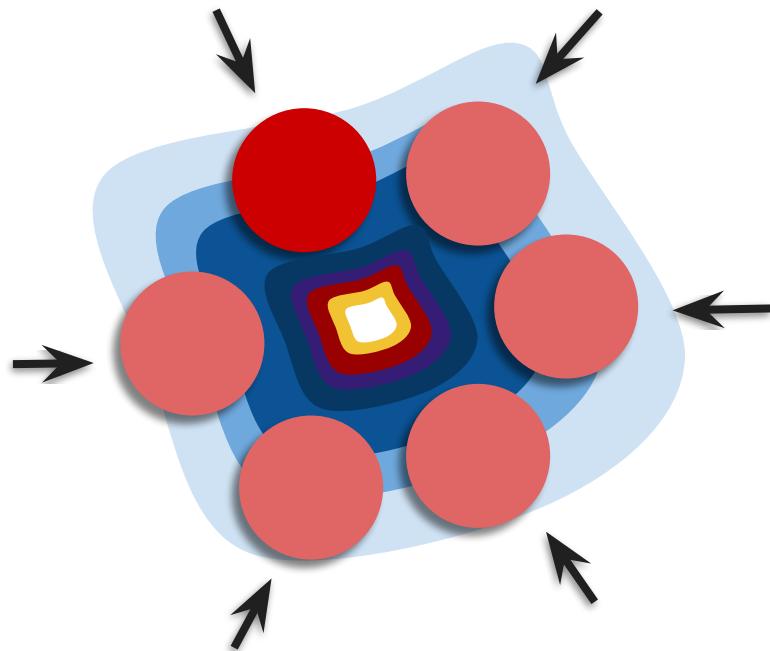


Forces are **attractive**
Needs thermostat to achieve equilibrium distribution
Must be used in MD

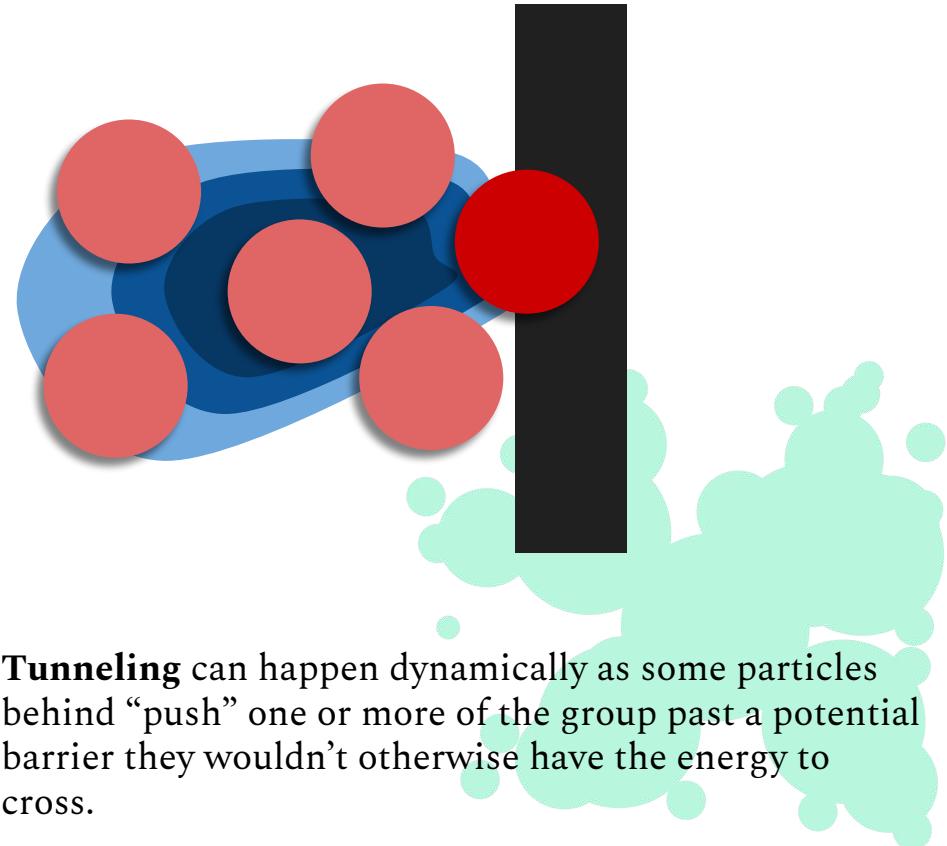


Forces are **repulsive**
If damped will simply relax to the ground state as an equilibrium
Can be used as geometry optimisation

Quantum effects in MIW

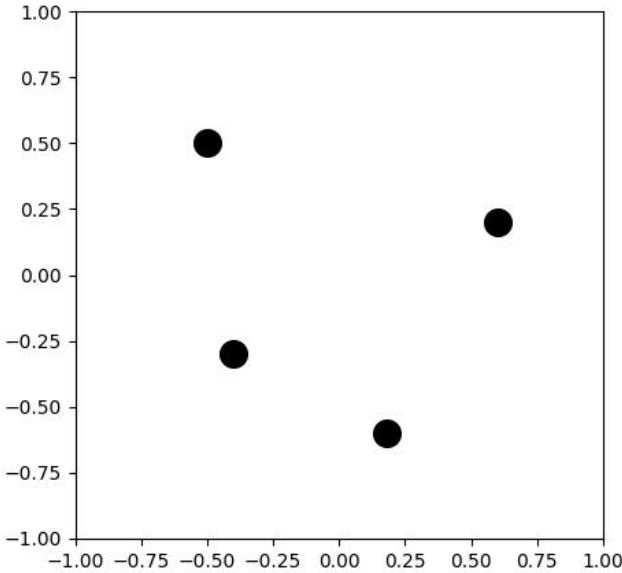


Delocalisation arises because as an external potential pushes inwards, a compressed bundle of particles is pushed back by the quantum potential, like a compressed gas.

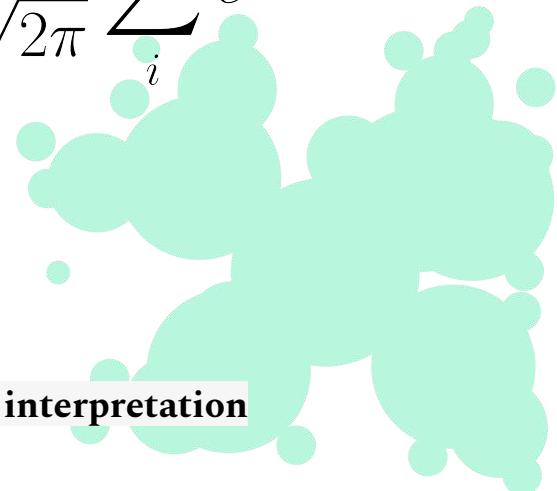


Tunneling can happen dynamically as some particles behind “push” one or more of the group past a potential barrier they wouldn’t otherwise have the energy to cross.

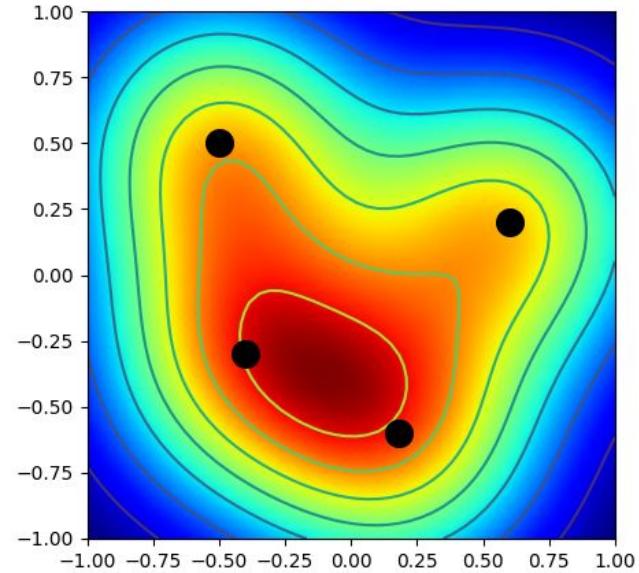
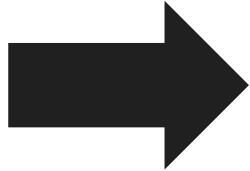
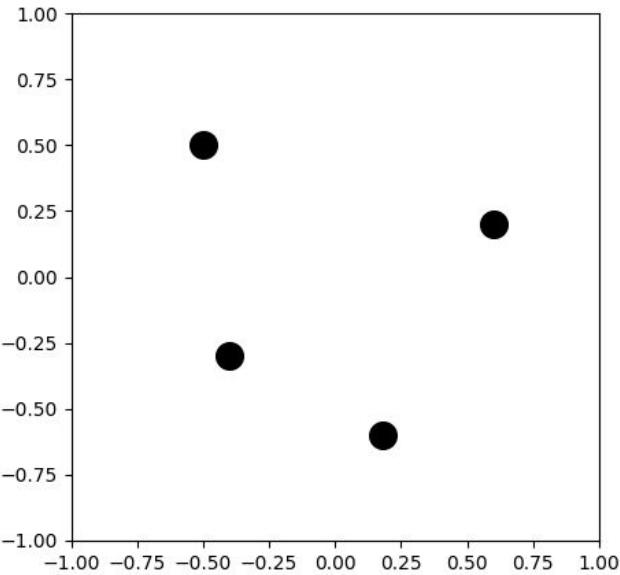
Probability density: the kernel approach



$$P(x) = \frac{1}{\sigma N \sqrt{2\pi}} \sum_i^N e^{-\frac{(x-x_i)^2}{2\sigma^2}}$$



Probability density: the kernel approach



Probability density: the kernel approach

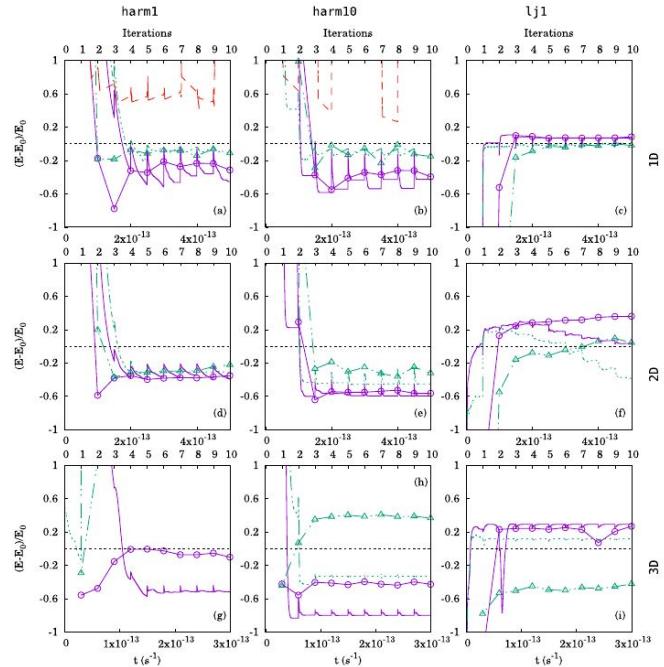


FIG. 3. Energy convergence during the relaxation process for different potentials and dimensionalities. Continuous lines represent the Gaussian kernel, dot-dashed lines the exponential one, and dashed lines the method from [13] converged with damped Langevin MD. Empty circles and triangles represent, respectively, the Gaussian and exponential kernels converged with the BFGS algorithm. For the labels, refer to the caption in Fig. 2.

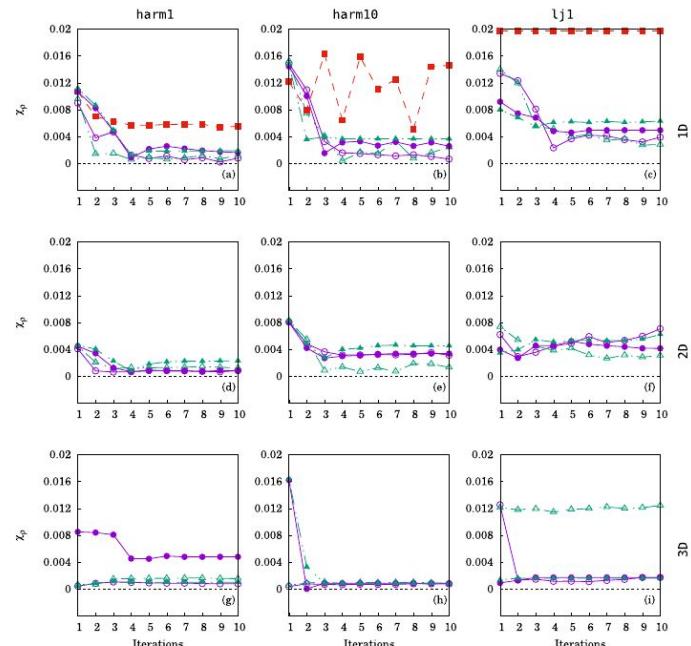


FIG. 4. Ground-state density error RSS convergence during the relaxation process for different potentials and dimensionalities. Circles represent the Gaussian kernel, and triangles represent the exponential one. Full markers represent damped MD, whereas empty ones represent BFGS. It was not possible to compute the quantity for the original method as it does not provide a continuous approximation for the density. For the labels, refer to the caption in Fig. 2.

Probability density: the kernel approach

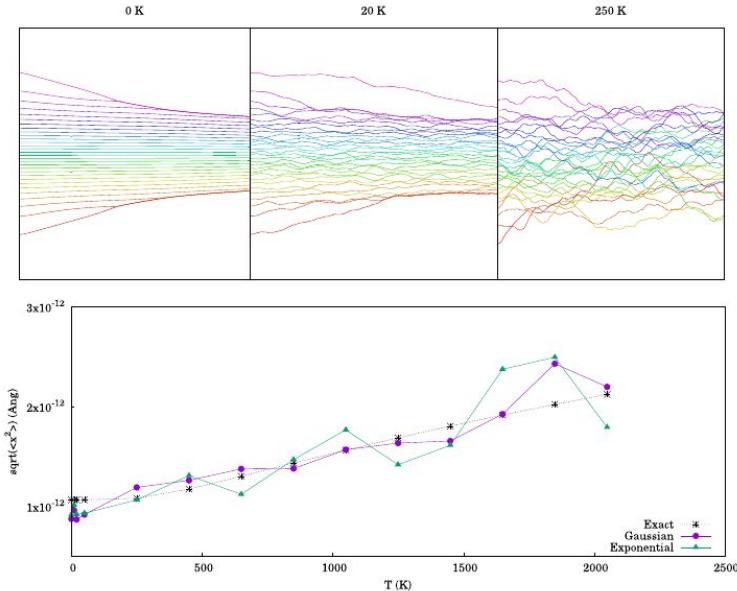


FIG. 5. Top: Many-interacting-world trajectories at different temperatures and computed value of $\sqrt{\langle x^2 \rangle}$ up to 2000 K for a particle in a harmonic oscillator with $k = 1 \text{ eV}/\text{\AA}^2$, using $N = 30$ MIW worlds and an exponential kernel. Bottom: standard deviation for theoretical and computed densities with Gaussian and exponential kernels as a function of temperature.

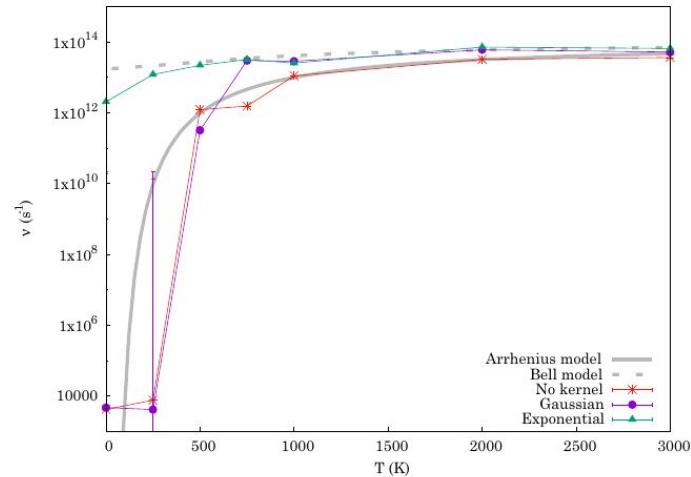


FIG. 7. Jumping rates in a MIW simulation on a double harmonic well potential. The fitted parameters are shown with error bars (though most of them are so small as to be invisible) and overlapped with the Arrhenius and Bell models.

Probability density: the harmonic approximation

“The career of a young theoretical physicist consists of treating the harmonic oscillator in ever-increasing levels of abstraction.”

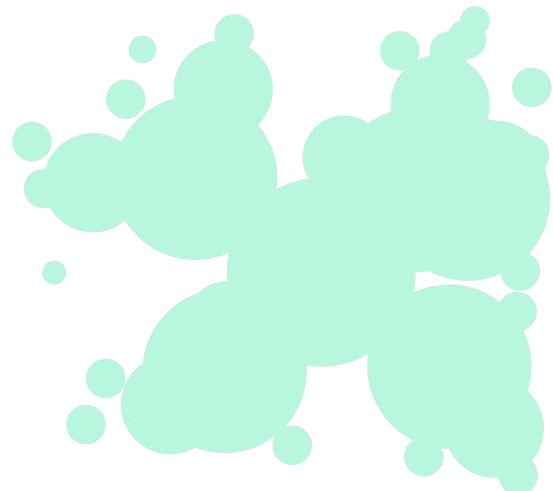
Sidney Coleman



Probability density: the harmonic approximation

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

$$V(x) = \frac{1}{2} k x^2$$



Probability density: the harmonic approximation

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

$$\langle V \rangle = \frac{1}{2}k(\mu^2 + \sigma^2)$$

$$V(x) = \frac{1}{2}kx^2$$

$$\langle K \rangle = \frac{1}{2}m(\dot{\mu}^2 + \dot{\sigma}^2)$$

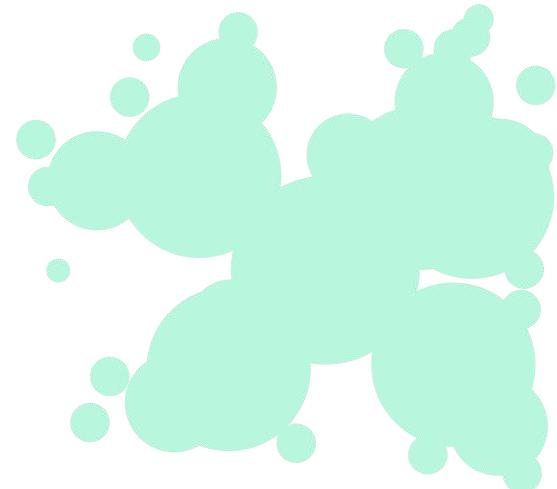
$$\langle U \rangle = \frac{\hbar^2}{8m}\frac{1}{\sigma^2}$$

Probability density: the harmonic approximation

$$m\ddot{\sigma} = k\sigma - \frac{\hbar^2}{4m}\frac{1}{\sigma^3} = 0$$



$$\sigma = \sqrt{\frac{\hbar}{2m\omega}}$$



Probability density: the harmonic approximation

$$\mathcal{L} = \langle K \rangle - \langle V \rangle - \langle U \rangle =$$

$$\frac{1}{2}m(\dot{\mu}^2 + \dot{\sigma}^2) - \frac{1}{2}k(\mu^2 + \sigma^2) - \frac{\hbar^2}{8m}\frac{1}{\sigma^2}$$

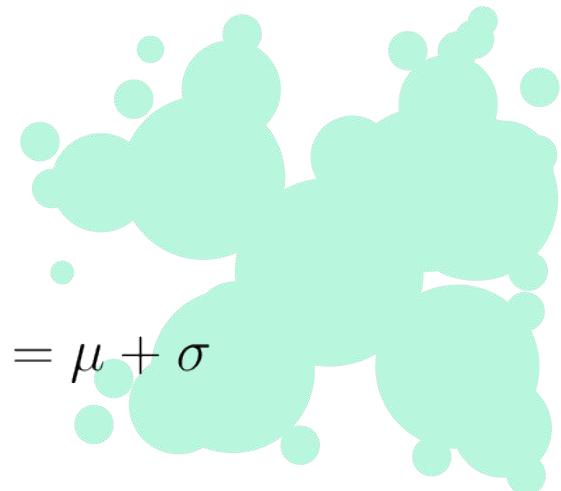


Probability density: the harmonic approximation

$$\mathcal{L} = \langle K \rangle - \langle V \rangle - \langle U \rangle =$$

$$\frac{1}{2}m(\dot{\mu}^2 + \dot{\sigma}^2) - \frac{1}{2}k(\mu^2 + \sigma^2) - \frac{\hbar^2}{8m}\frac{1}{\sigma^2}$$

$$x_- = \mu - \sigma \qquad \qquad \frac{\hbar^2}{m} \frac{1}{r^2} \qquad \qquad x_+ = \mu + \sigma$$



Probability density: the harmonic approximation

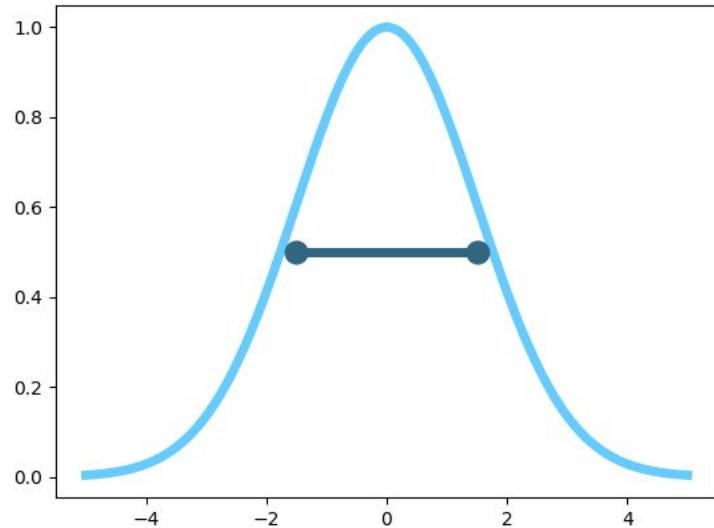
$$\mathcal{L} = \langle K \rangle - \langle V \rangle - \langle U \rangle =$$

$$\frac{1}{2}m(\dot{\mu}^2 + \dot{\sigma}^2) - \frac{1}{2}k(\mu^2 + \sigma^2) - \frac{\hbar^2}{8m}\frac{1}{\sigma^2}$$

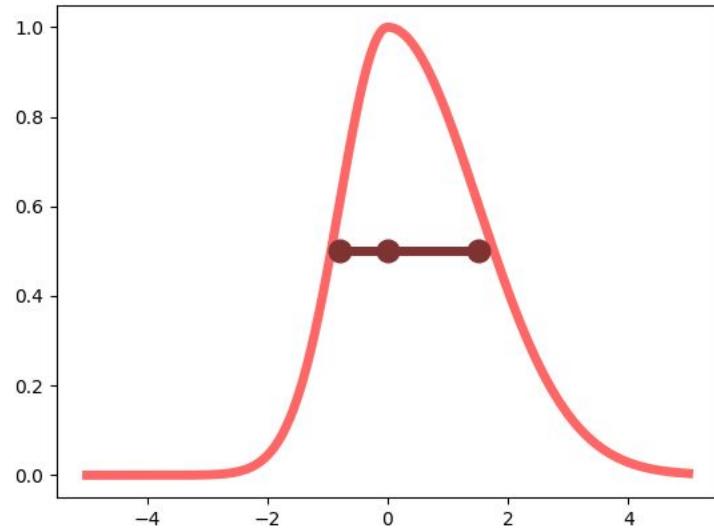
$$\tilde{\mathcal{L}} = \frac{1}{2}m(\dot{x}_+^2 + \dot{x}_-^2) - \frac{1}{2}k(x_+^2 + x_-^2) - \frac{\hbar^2}{m}\frac{1}{(x_+ - x_-)^2}$$

$$= m(\dot{\mu}^2 + \dot{\sigma}^2) - k(\mu^2 + \sigma^2) - \frac{\hbar^2}{4m}\frac{1}{\sigma^2}$$

Symmetric and asymmetric stencils

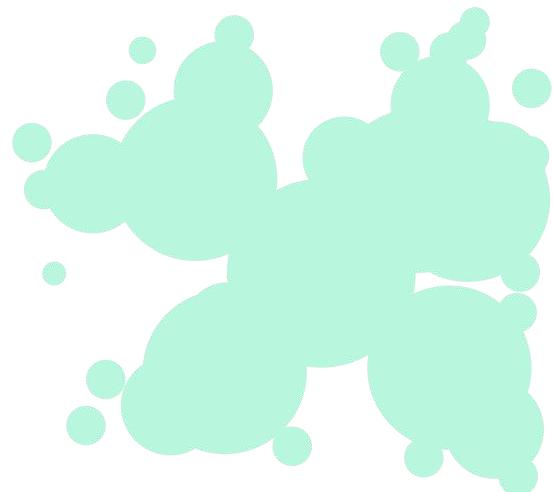


μ, σ

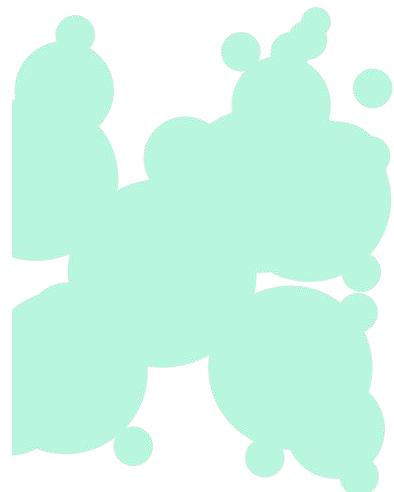
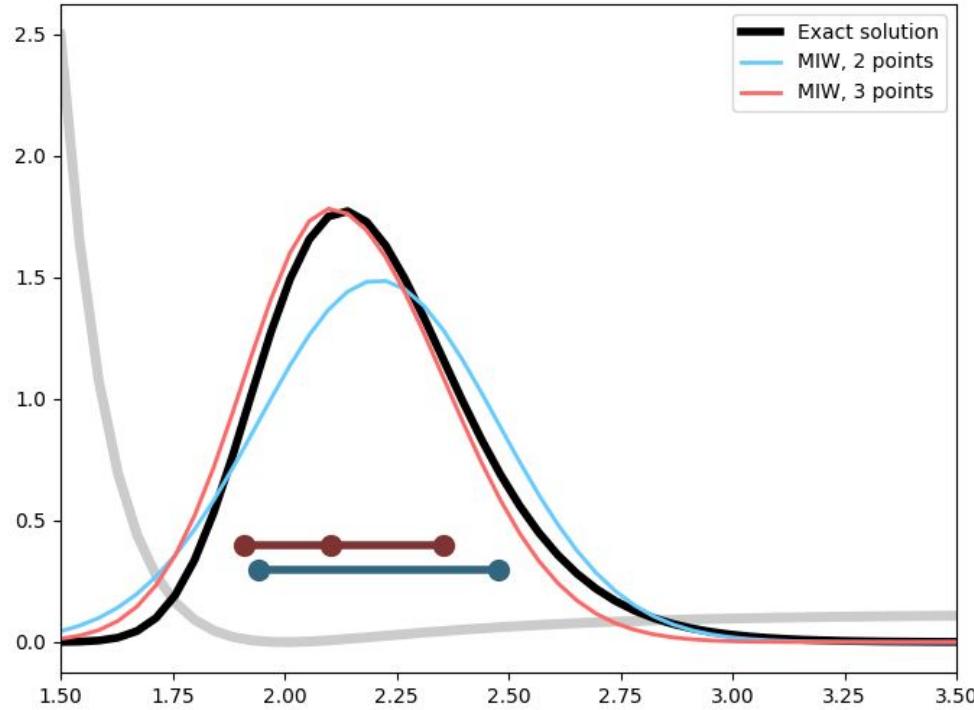


μ, σ_+, σ_-

1D harmonic stencil - Examples



Ground state approximation - LJ 1D



N-Dimensional case

$$P(\mathbf{x}) = \frac{1}{\sqrt{(2\pi)^n |\Sigma|}} e^{-\frac{1}{2}(\mathbf{x}-\mathbf{x}_0)\Sigma^{-1}(\mathbf{x}-\mathbf{x}_0)}$$

$$V(\mathbf{x}) = \frac{1}{2}\mathbf{x}K\mathbf{x}$$

$$J = m [\text{Tr}(\Sigma)\mathbb{I} - \Sigma]$$

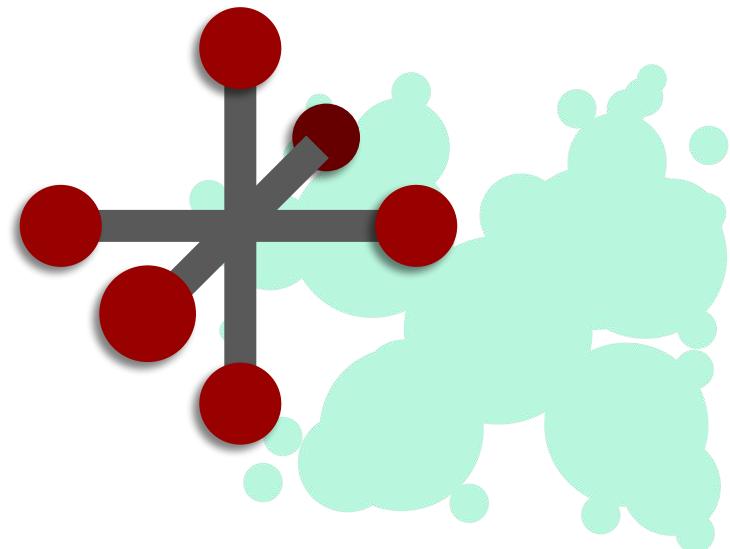
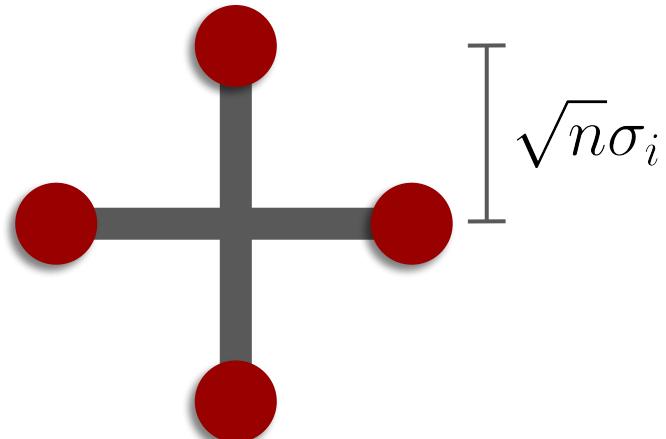
$$\langle V \rangle = \frac{1}{2} [\mathbf{x}_0 K \mathbf{x}_0 + \text{Tr}(\Sigma K)]$$

$$\langle K \rangle = \frac{1}{2}m \left(\dot{\mathbf{x}}^2 + \sum_i^n \dot{\sigma}_i^2 \right) + \frac{1}{2}\omega J\omega$$

$$\langle U \rangle = \frac{\hbar^2}{8m} \text{Tr}(\Sigma^{-1})$$

N-Dimensional case

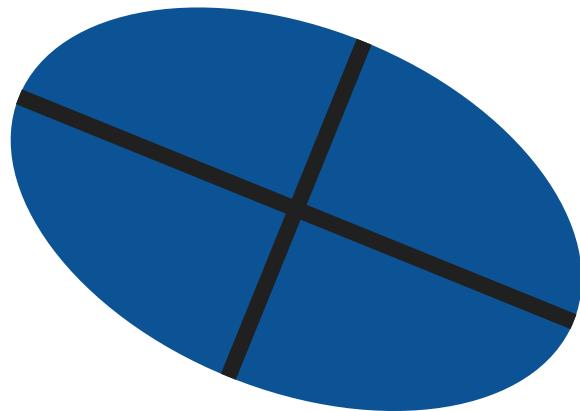
$$\mathcal{L} = \frac{1}{2}m \left(\dot{\mu}^2 + \sum_i \dot{\sigma}_i^2 \right) + \frac{1}{2}\omega \mathbf{J}\omega - \frac{1}{2}\text{Tr}(\Sigma K) - \frac{\hbar^2}{8m} \sum_i \frac{1}{\sigma_i^2}$$



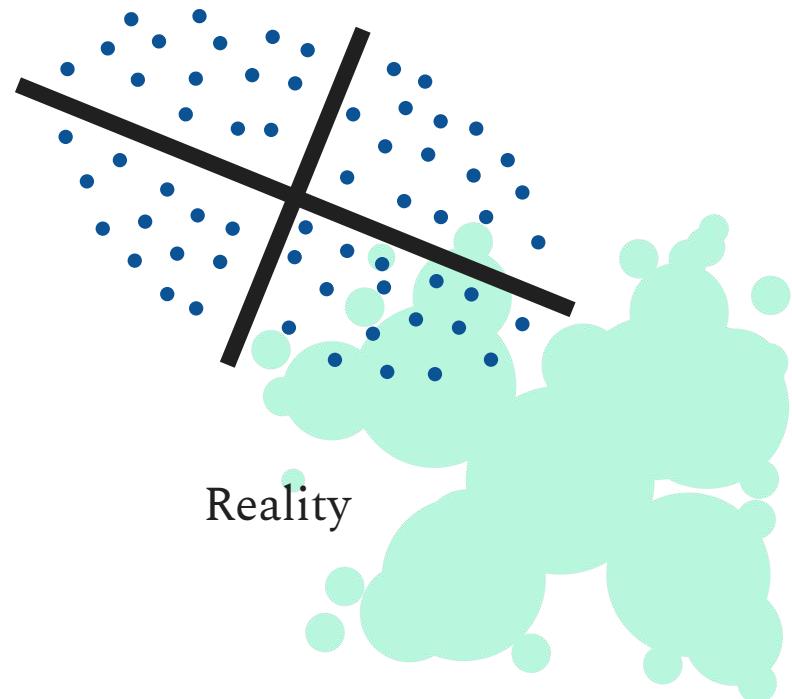
2D harmonic stencil - Examples



The rigid body problem

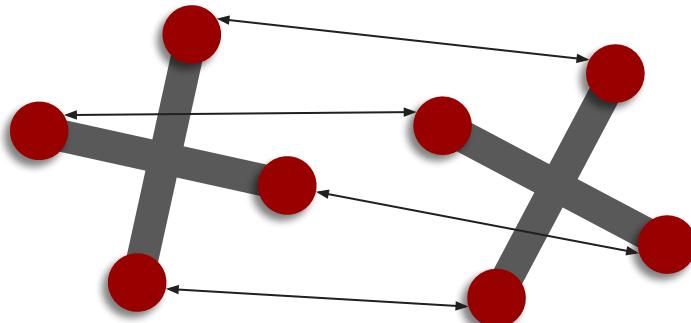


Approximation

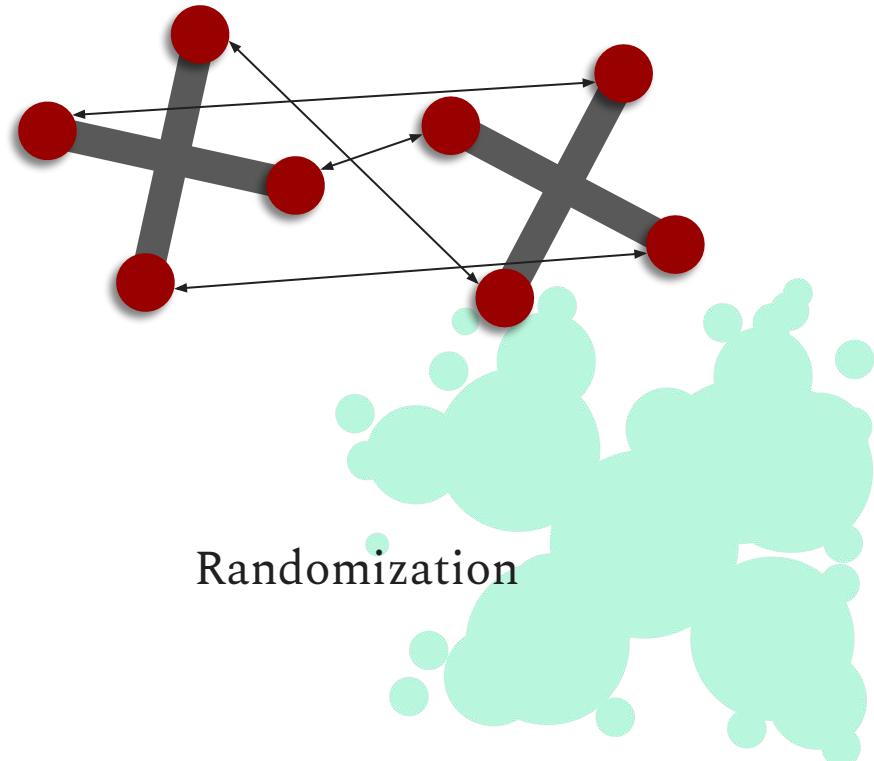


Reality

What about N-body systems?



1-to-1 correspondence



Randomization

Possibilities for future developments

- 6-point stencils for perfectly Gaussian distributions in 3D are an easy implementation; they could safely identify a ground state for a single quantum nucleus with a geometry optimisation (far faster than PIMD)
- 7-point stencils should also be straightforward to implement and allow for a lot more distributions
- Good real time dynamics in 3-D systems might be trickier as they would require going past the rigid body approximation
- N-body solutions still to test
- Easy implementations using classical force fields, DFTB or DFT backends for testing could be written in Python with ASE



Thanks for your attention!

