# Nuclear quantum dynamics simulation

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Winter school on Theoretical Chemistry and Spectroscopy
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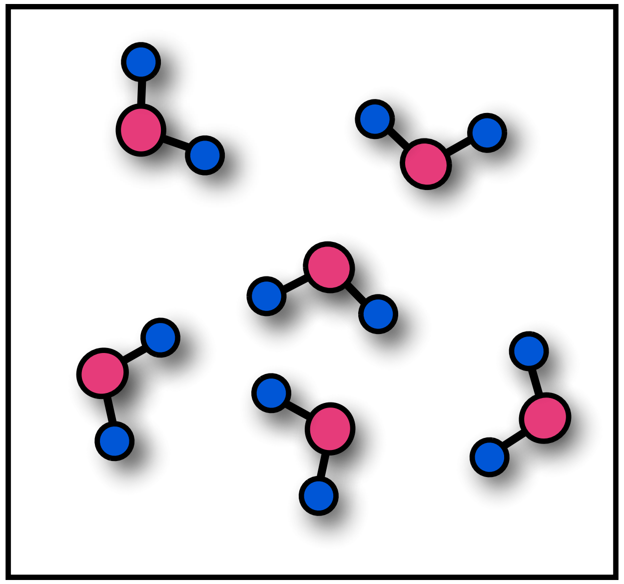
# Classical molecular dynamics



Molecular dynamics (MD) simulation

Sampling the distribution and the dynamics of many-particle systems

$$\langle A \rangle = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' A(\mathbf{r}^N, \mathbf{p}^N)$$

time averages equal the ensemble averages (ergodicity hypothesis)

$$\langle A \rangle = \frac{\iint d\mathbf{r}^N d\mathbf{p}^N A(\mathbf{r}^N, \mathbf{p}^N) \exp[-\beta H(\mathbf{r}^N, \mathbf{p}^N)]}{\iint d\mathbf{r}^N d\mathbf{p}^N \exp[-\beta H(\mathbf{r}^N, \mathbf{p}^N)]}$$

(N,V,T) ensemble

Newtonian equation of motion:

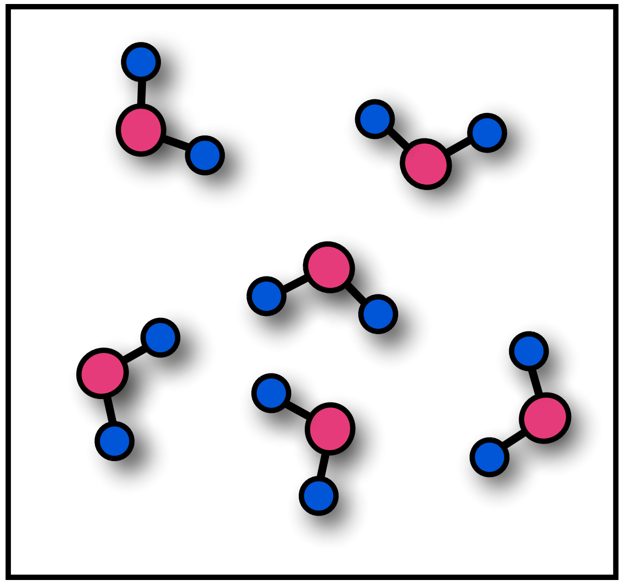
$$-\frac{dV}{dr_i} = m_i \frac{d^2 r_i}{dt^2}$$

Velocity verlet integrator:

$$x(t+\Delta t) = x(t) + v(t)\Delta t + a(t)\frac{(\Delta t)^2}{2}$$

$$v(t+\Delta t) = v(t) + \frac{[a(t) + a(t+\Delta t]}{2}\Delta t$$

# Classical molecular dynamics



Molecular dynamics (MD) simulation

Sampling the distribution and the dynamics of many-particle systems

Classical MD means:

1. Newtonian dynamics of the nuclei
2. Interaction potentials are sums of empirical (pair) potentials (forcefield)

$$E^{\text{pot}} = E^{\text{bonded}} + E^{\text{non-bonded}}$$

$$E^{\text{pot}} = \sum_{\text{bonds}} V^{\text{bond}} + \sum_{\text{angles}} V^{\text{angle}} \sum_{\text{dihedrals}} V^{\text{torsion}} + \sum_{\text{i}} \sum_{\text{j}\neq\text{i}} V^{\text{LJ}} + \sum_{\text{i}} \sum_{\text{j}\neq\text{i}} V^{\text{Coulomb}}$$

$$V^{\text{harm}}(r) = \frac{1}{2} k_b (r - r_0)^2$$

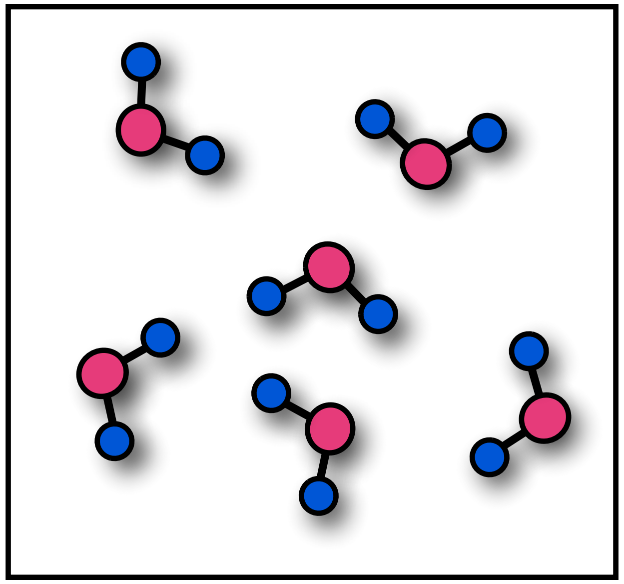
$$V^{\text{harm}}(\theta) = \frac{1}{2} k_\alpha (\theta - \theta_0)^2$$

$$V^{\text{Fourier}}(\omega) = \sum_n \frac{1}{2} V_n [1 + \cos(n\omega - \gamma)]$$

$$V^{\text{LJ}}(r) = -4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right)$$

$$V^{\text{Coulomb}}(r) = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$$

# Classical molecular dynamics



Molecular dynamics (MD) simulation

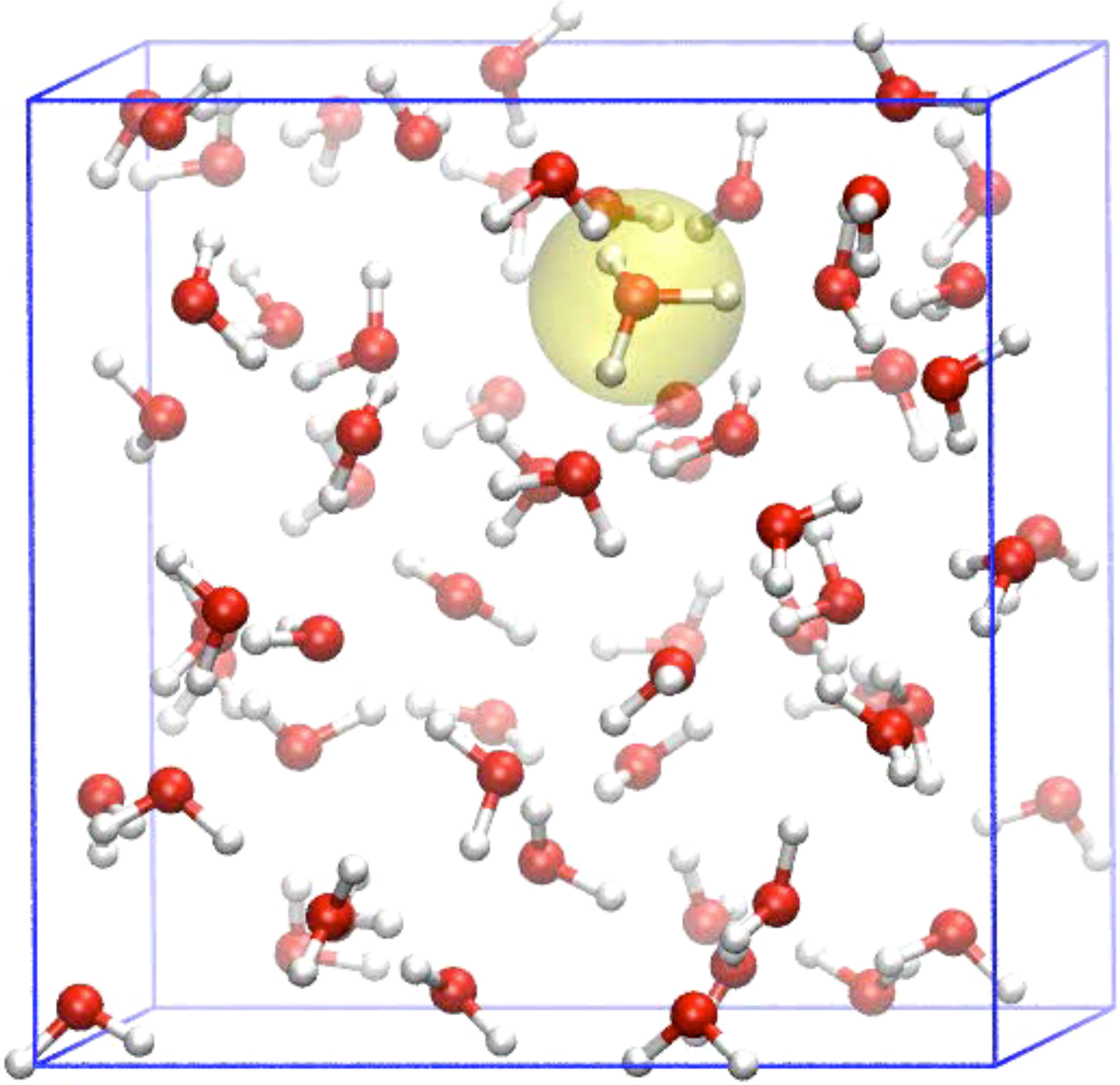
Sampling the distribution and the dynamics of many-particle systems

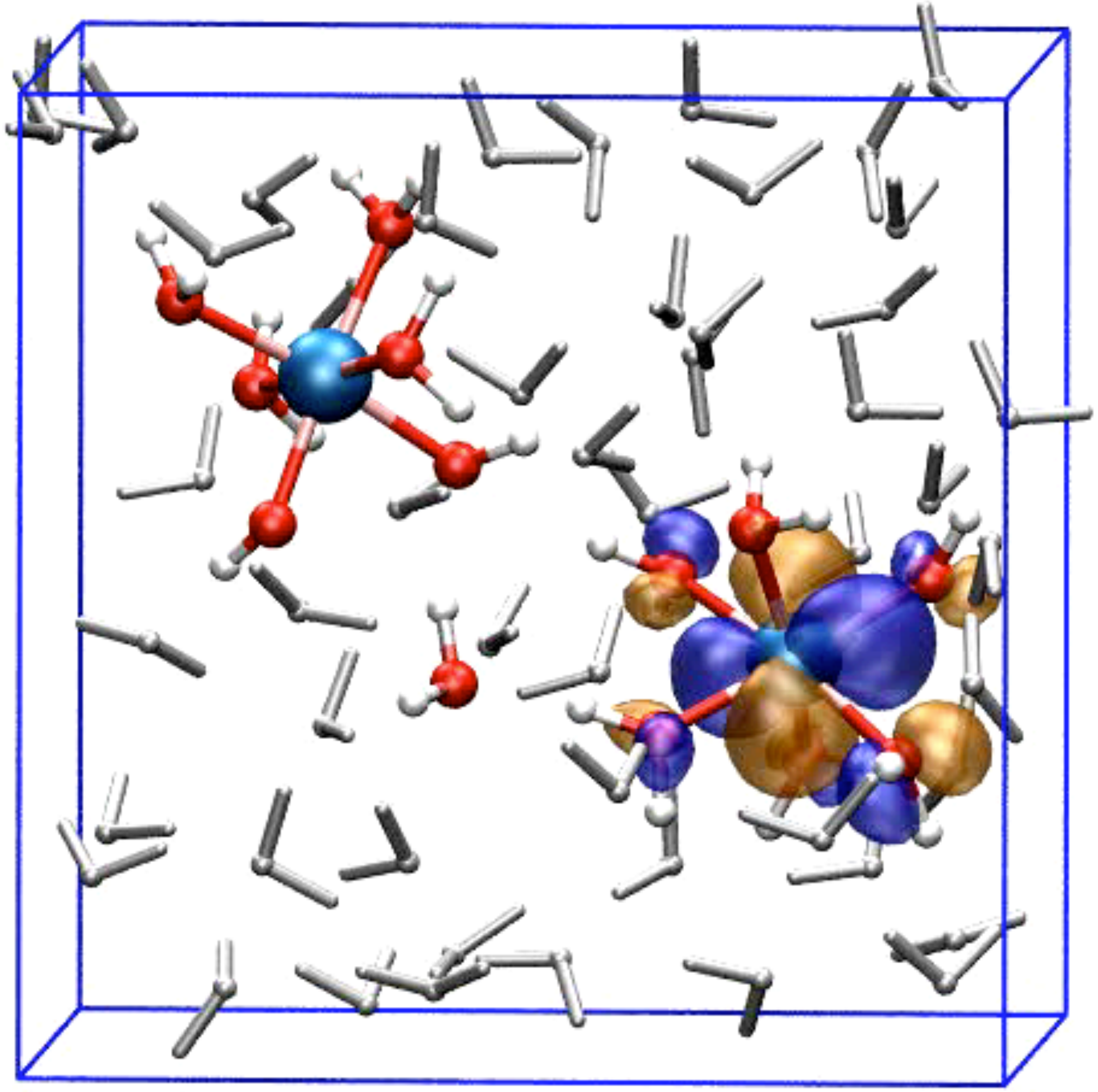
Ab initio MD, First principles MD, DFT-MD, Born-Oppenheimer MD, Car-Parrinello MD

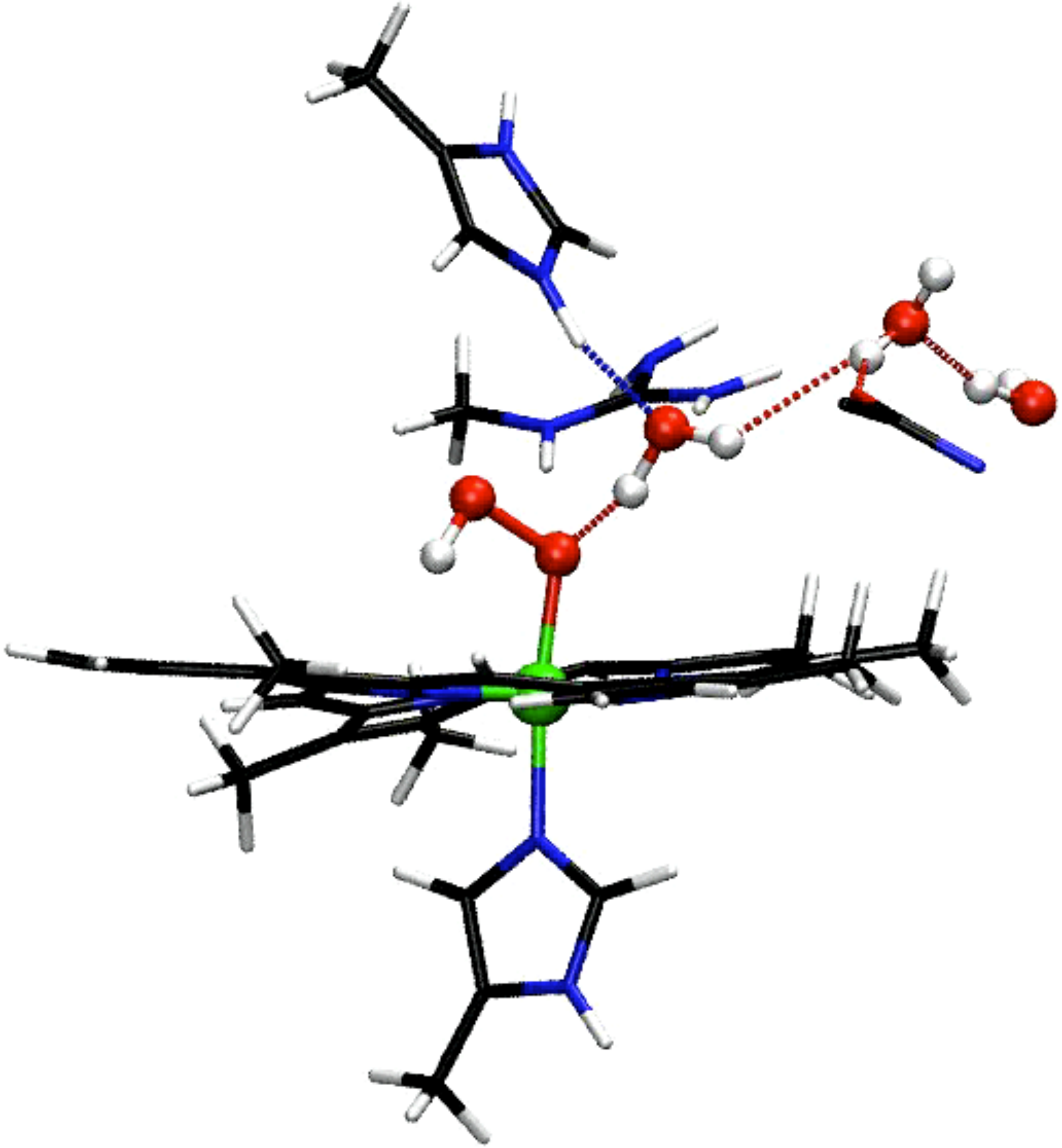
- Interaction potential from electronic structure calculation
- quantum mechanical description of the electronic structure (DFT)
- Born-Oppenheimer approximation (electronic ground-state)
- Nuclear dynamics is still Newtonian!

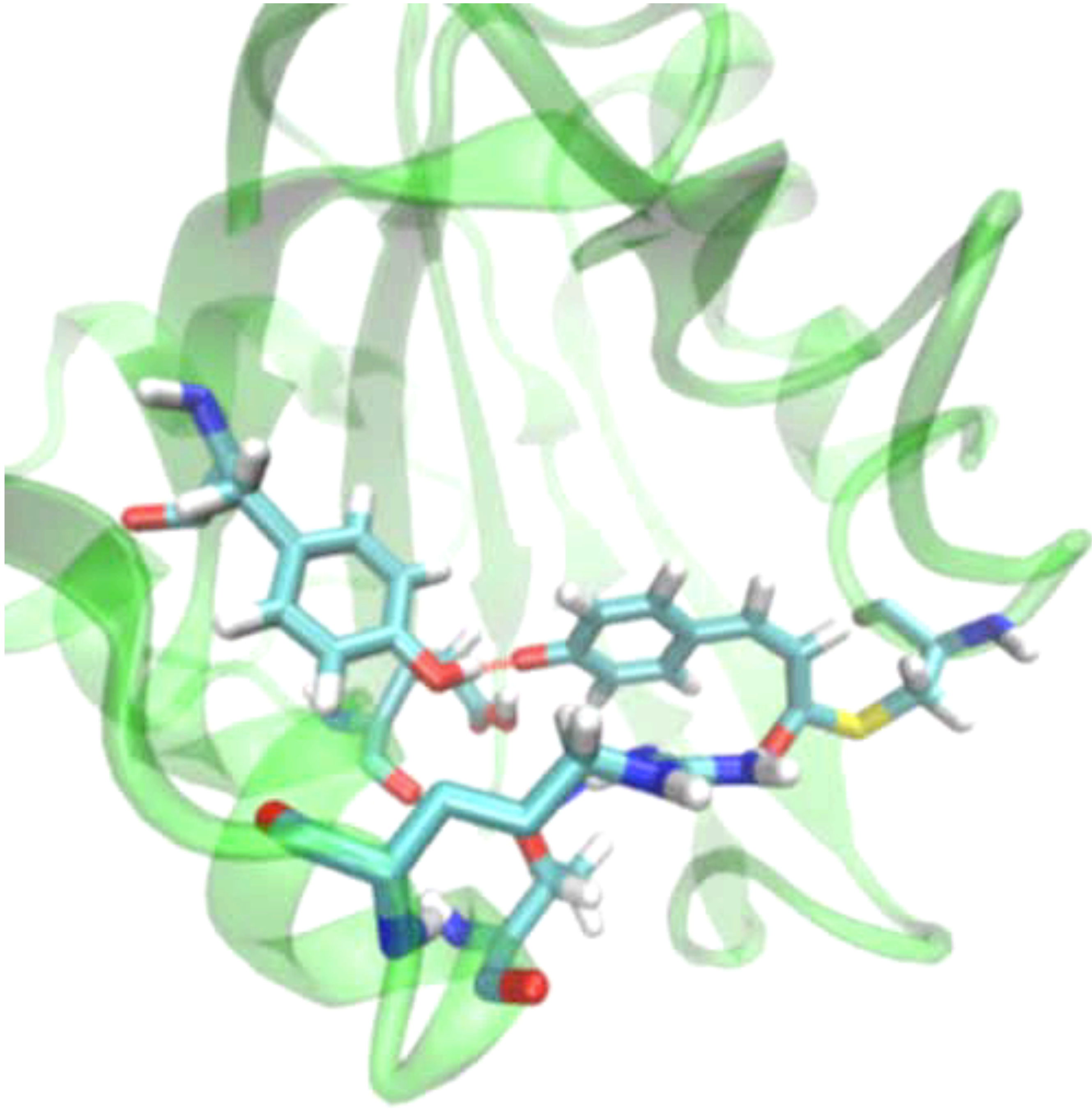
$$H = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 + \frac{1}{4\pi\epsilon_0}\sum_{i<j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0}\sum_{I,i}\frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{4\pi\epsilon_0}\sum_{I<J}\frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|}$$

$$M_I \frac{d^2\mathbf{R}}{dt^2} = -\nabla_I \min_{\psi_0}\{\langle\psi_0|H_e|\psi_0\rangle\}$$

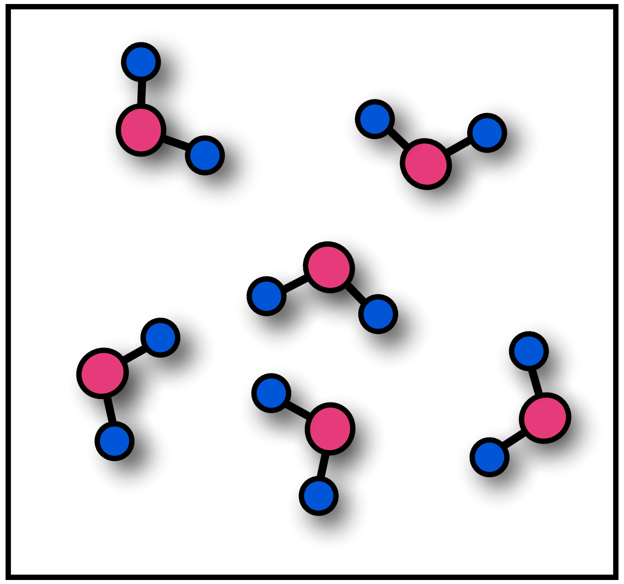








# Nuclear quantum effects



Molecular dynamics (MD) simulation

Sampling the distribution and the dynamics of many-particle systems

Classical (forcefield) MD and ab initial (DFT) MD both neglect nuclear quantum effects.

- zero point energy motion (ZPE)
- quantum tunneling

The problem is worse for AIMD as in the case of empirical forcefields fitted to experimental quantities, NQEs are implicitly included.

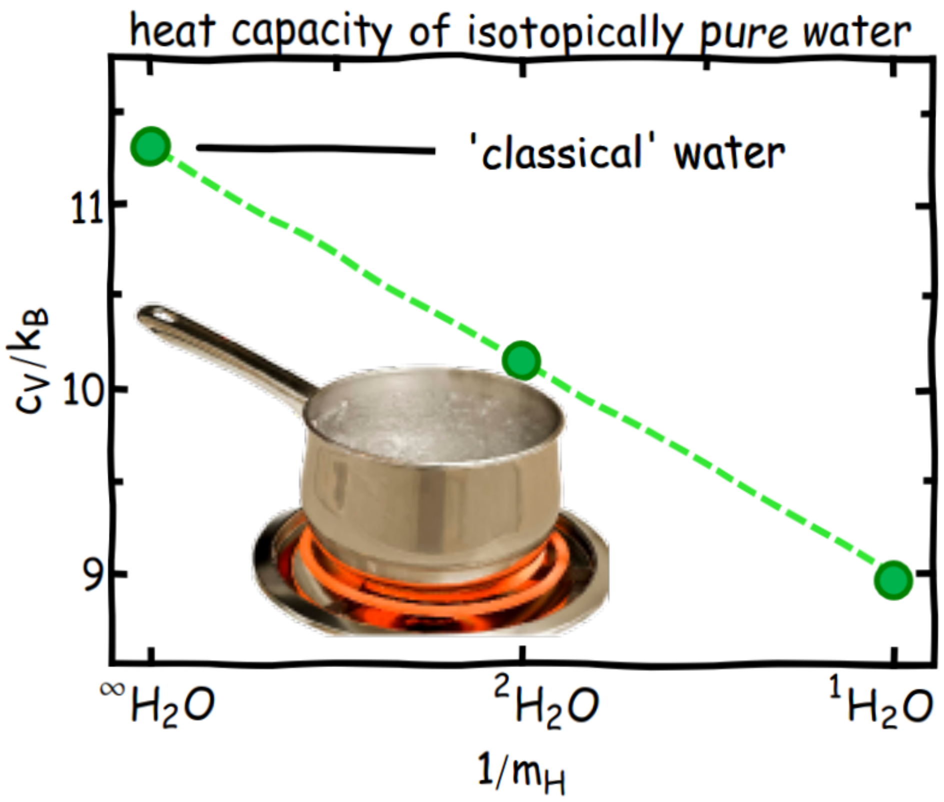
# Nuclear quantum effects

Newtonian dynamics is inaccurate for:

- light particles
- very low temperatures
- large spacing of energy levels, $\hbar\omega > k_B T$

Nuclear quantum effects affect, even at room temperature, e.g.:

- heat capacity of materials
- isotope effects (KIE) on reaction rates, especially involving proton or hydrogen transfer



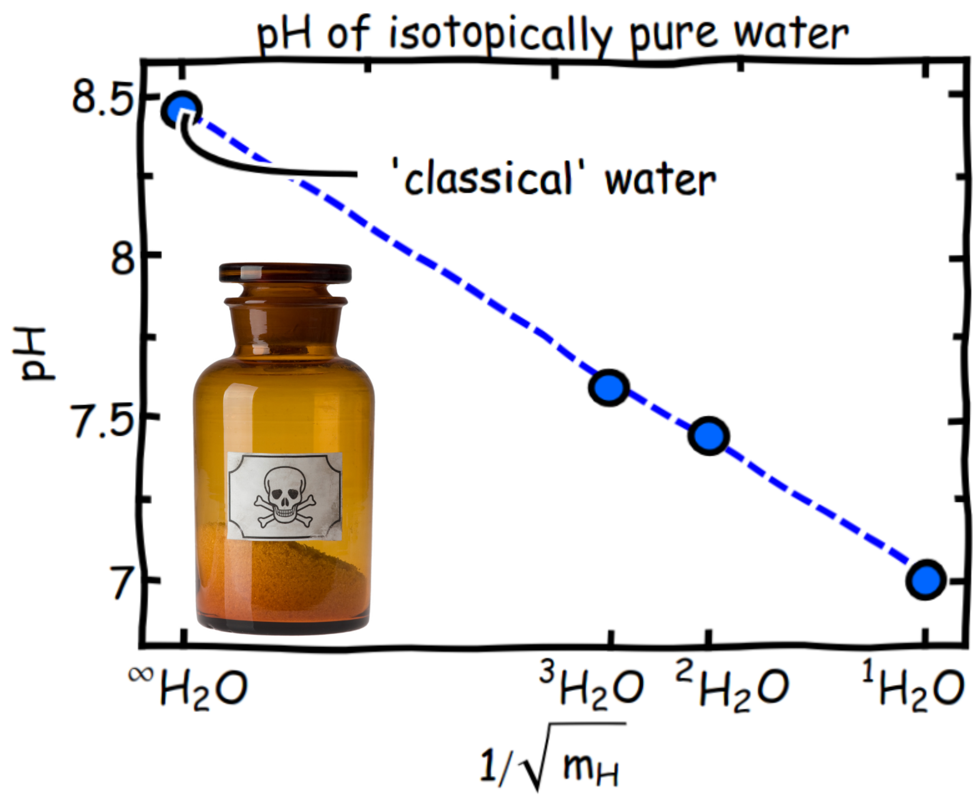


figure thanks to Michele Ceriotti (EPFL)

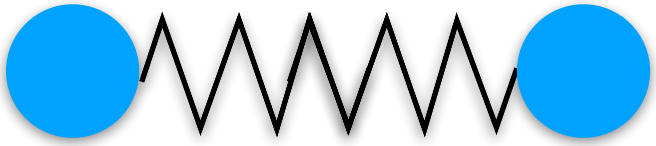
# Path integral molecular dynamics

## the general idea

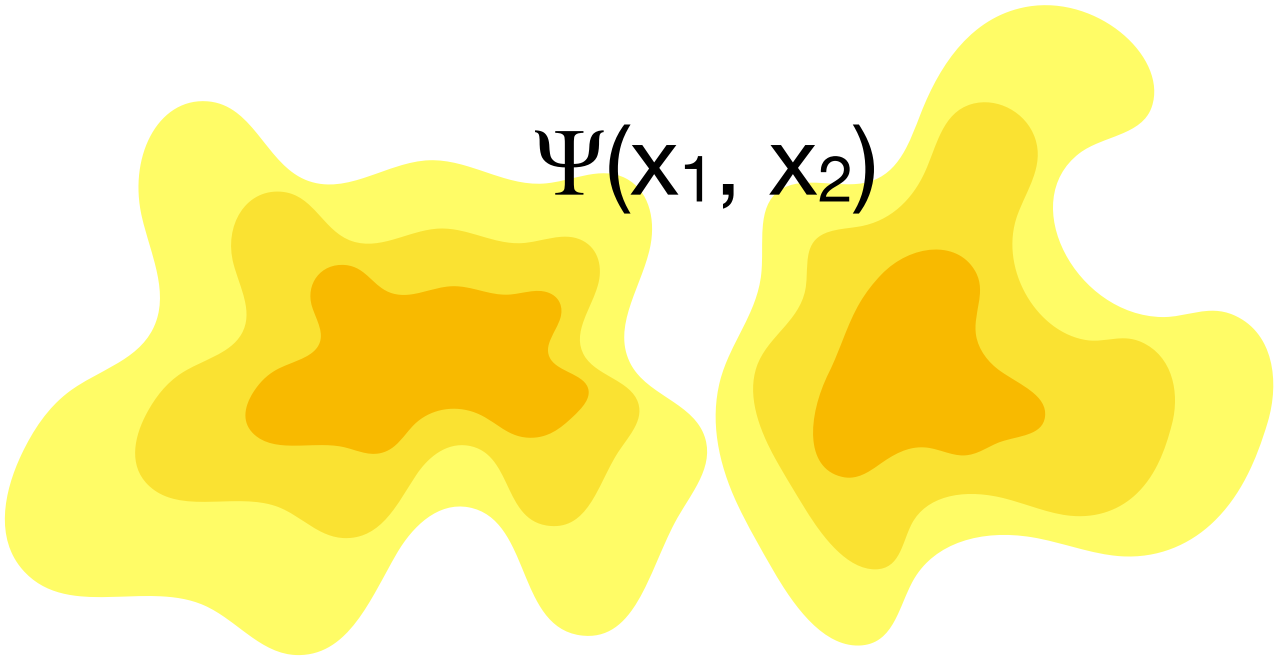
- solving the Schrödinger equation for the whole system is too impractical
- there quantum statistics of particles can be represented by the classical dynamics of a “ring polymer”

$$\mathcal{H}_{cl,P}(x,p) = \sum_{k=1}^{P}\left[\frac{p_k^2}{2m} + \frac{m}{2\beta_P^2\hbar^2}\sum_{k=1}^{P}(x_k - x_{k+1})^2 + \sum_{k=1}^{P}U(x_k)\right]$$

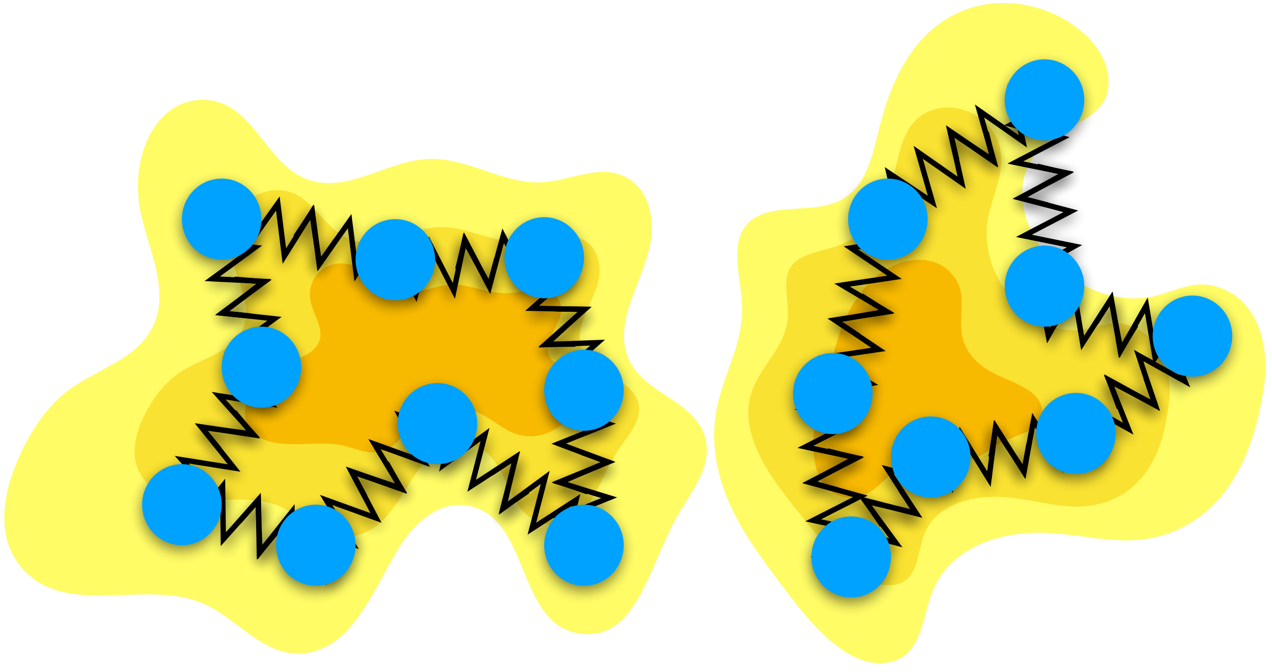
*p* is the number of beads



classical particles



quantum



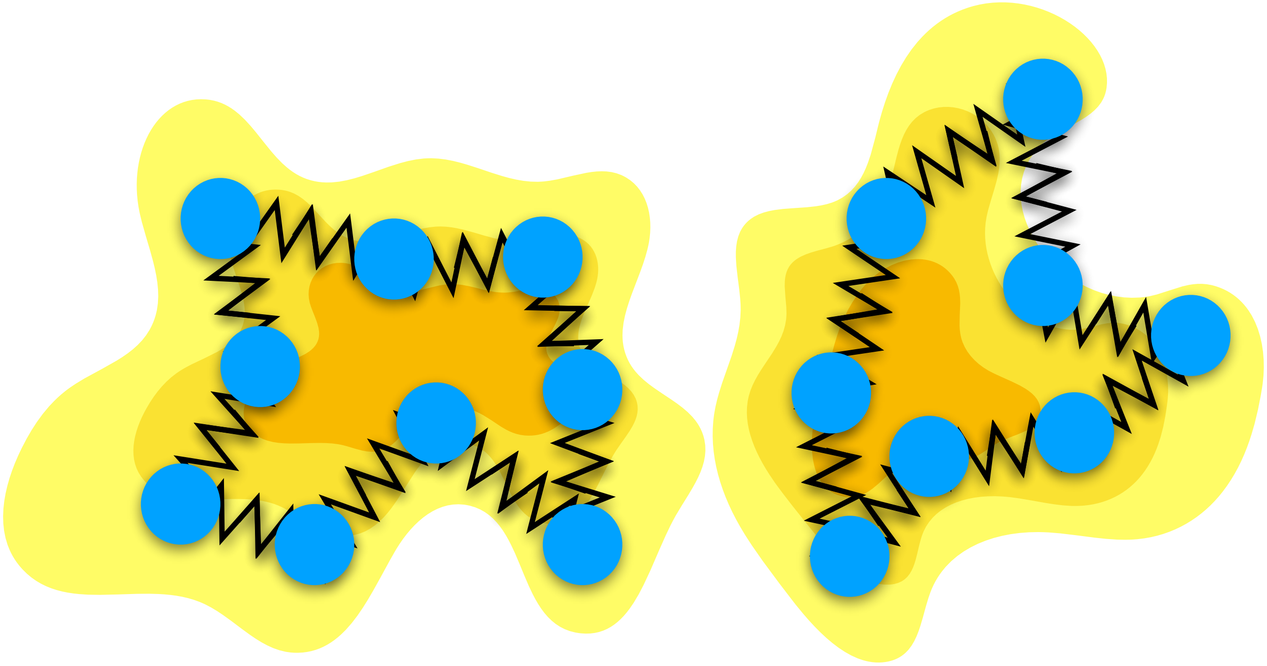
path-integrals as ring polymers

# Ring polymer dynamics

## the general idea

- solving the Schrödinger equation for the whole system is too impractical
- there quantum statistics of particles can be represented by the classical dynamics of a “ring polymer”

- Ring polymers represent imaginary time path integrals
- Capture tunneling and ZPE effects on equilibrium properties
- Can be extended to capture quantum dynamics
- Can be extended to include quantum exchange (indistinguishable particles)



path-integrals as ring polymers

- Why nuclear quantum dynamics?
- Feynman path integral formulation
- Centroid molecular dynamics
- Ring polymer molecular dynamics
- Time correlation functions (quantum dynamics)
- Ceriotti approach (coloured noise)
- Some applications

# Quantum mechanical time evolution (Schrödinger picture)

Time dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi(t) = \hat{H}\Psi(t)$$

Wave function (or state vector) evolves in time; operators connected to observables are static

solve the first-order differential equation

$$\Psi(t) = e^{-i\hat{H}t/\hbar}\Psi(0)$$

$$x(t) = e^{iLt}x(0)$$

NB classical propagation by Liouville operator

define the quantum propagator, a unitary operator

$$\hat{U}(t) = e^{-i\hat{H}t/\hbar}$$

$$\hat{U}^\dagger(t)\hat{U}(t) = \hat{I}$$

$$|\Psi(t)|^2 = 1$$

it will not change the magnitude of the state vector, only its direction

For example:

$$\Psi(0) = \sum_k |E_k\rangle\langle E_k|\Psi(0)\rangle$$

with the eigenvalues E$_k$ $\hat{H}|E_k\rangle = E_k|E_k\rangle$

then the time evolution of the amplitudes is $\Psi(t) = \sum_k e^{-i\hat{H}t/\hbar}|E_k\rangle\langle E_k|\Psi(0)\rangle$

NB calculation of the eigenvalues and eigenvectors is difficult and only possible for very small systems (as we all know very well)

# Quantum mechanical time evolution (Heisenberg picture)

In Heisenberg picture, the observable operator evolves in time (state vector is static) :

$$\frac{d\hat{A}}{dt} = \frac{-i}{\hbar}[\hat{A},\hat{H}]$$

*Heisenberg equation of motion*

commutator:

$$[\hat{A},\hat{H}] = \hat{A}\hat{H} - \hat{H}\hat{A}$$

NB: very similar to classical evolution of a phase-space function, using the Poisson bracket $\frac{dA}{dt} = \{\hat{A},\hat{H}\}$

Solution: $\hat{A}(t) = e^{i\hat{H}t/\hbar}\hat{A}(0)e^{-i\hat{H}t/\hbar} = \hat{U}^{\dagger}(t)\hat{A}(0)\hat{U}(t)$

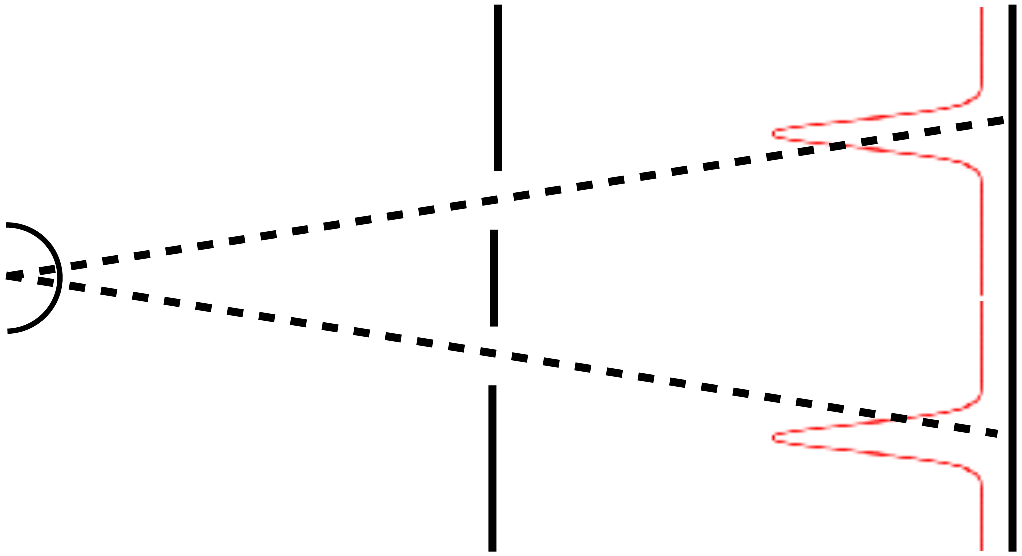
Expectation value: $\langle\hat{A}(t)\rangle = \langle\Psi|\hat{A}(t)|\Psi\rangle$

NB if $\hat{A}$ commutes with the Hamiltonian $\hat{H}$ then $\frac{d\hat{A}}{dt} = 0$ , $\hat{A}$ is a *constant of motion*.

# Quantum mechanical time evolution (Feynman path integrals)

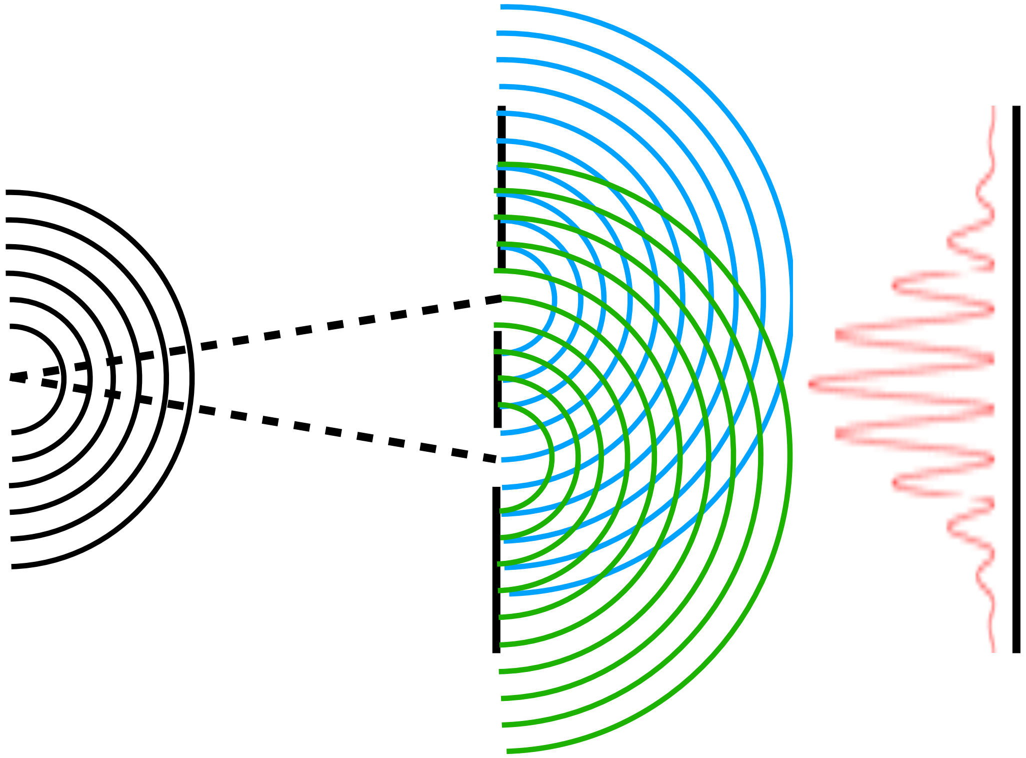
## The double slit experiment

classical particles



two target distributions

quantum mechanical particles

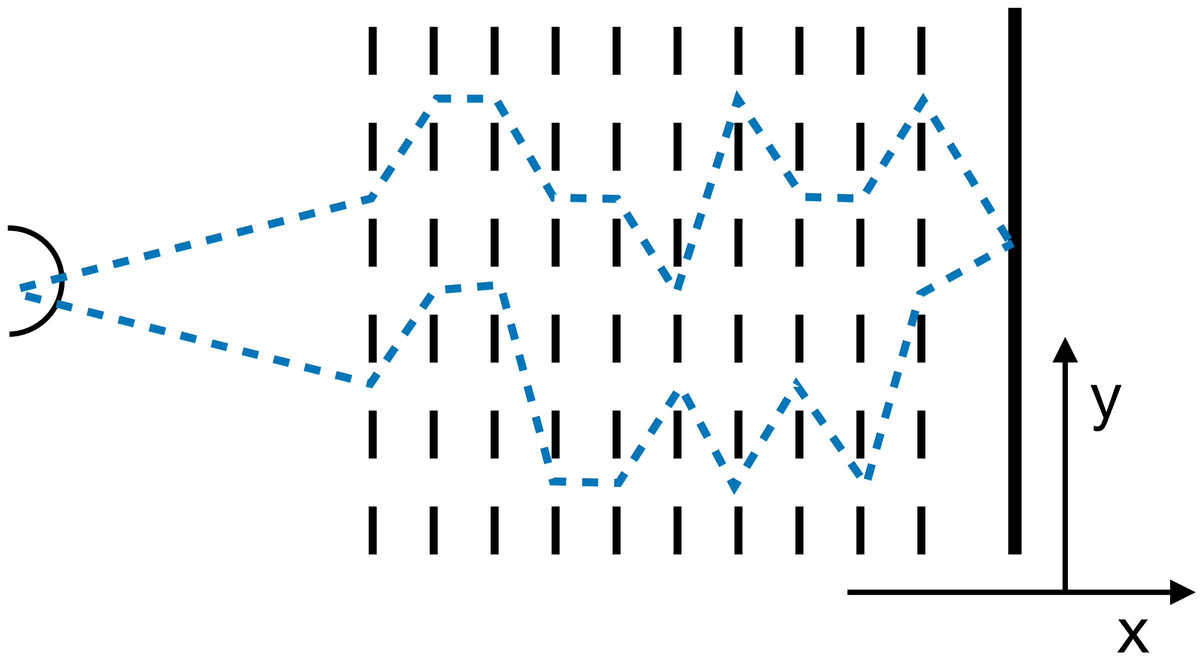


interference pattern

# Quantum mechanical time evolution (Feynman path integrals)

## The double slit experiment

Feynman's idea



two possible paths in an experiment with many slits in many screens

- Each path has an amplitude $A_i(y)$

$A_i$ is the amplitude that the electron, following path i, has on the detector at position y.

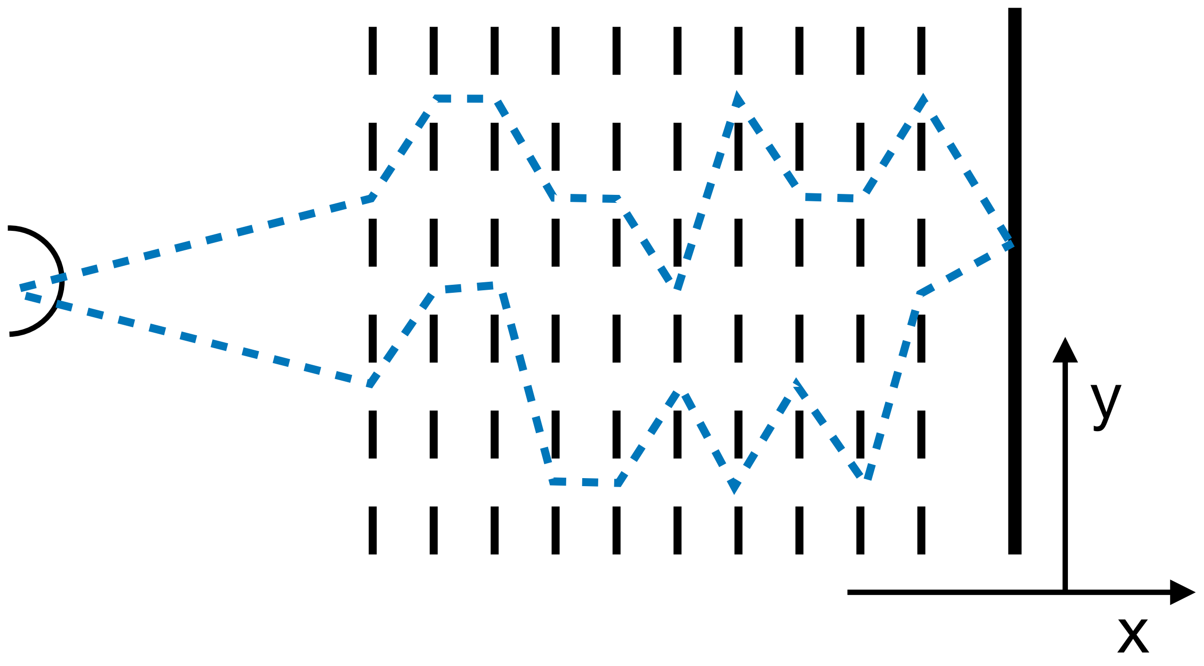
- Total amplitude at y: $A(y) = A_1(y) + A_2(y) + A_3(y) + \ldots$
- The probability at y: $P(y) = |A(y)|^2 = |A_1(y) + A_2(y) + A_3(y) + \ldots|^2$
- For 2 paths: $P(y) = |A(y)|^2 = |A_1(y) + A_2(y)|^2$
- complex amplitudes: $A_1(y) = |A_1| \exp[i\Phi_1(y)]$ and $A_2(y)=|A_2| \exp[i\Phi_2(y)]$
- Therefore: $P(y) = |A_1(y)|^2 + |A_2(y)|^2 + 2\,|A_1(y)|\,|A_2(y)| \cos[\Phi_1(y)-\Phi_2(y)]$

third term is the interference between the two paths

# Quantum mechanical time evolution (Feynman path integrals)

## The double slit experiment

Feynman's idea



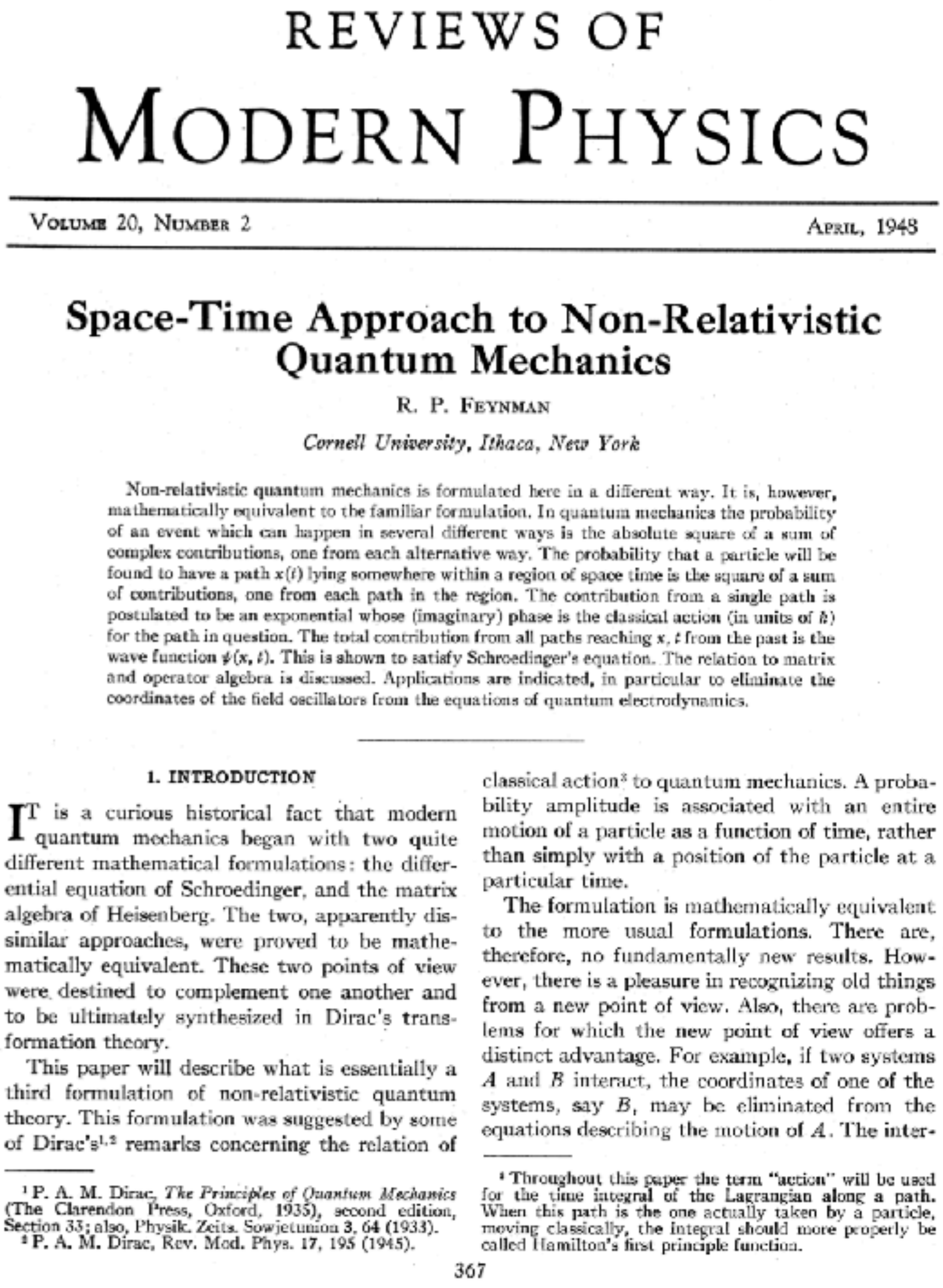
two possible paths in an experiment with many slits in many screens

All possible paths have to be included to obtain the correct probability.
The number of interference terms grows to infinite.

$$P(y) = \left| \sum_{\text{paths}} A_{\text{path}}(y) \right|^2$$

Imagine the number of screens and slits to increase until infinite.
However, the space between the slits goes to zero; the grating disappears.

Feynman's idea: in empty space an (undetected) electron takes all possible paths!



REVIEWS OF
MODERN PHYSICS

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# Space-Time Approach to Non-Relativistic Quantum Mechanics

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Non-relativistic quantum mechanics is formulated here in a different way. It is, however, mathematically equivalent to the familiar formulation. In quantum mechanics the probability of an event which can happen in several different ways is the absolute square of a sum of complex contributions, one from each alternative way. The probability that a particle will be found to have a path $x(t)$ lying somewhere within a region of space time is the square of a sum of contributions, one from each path in the region. The contribution from a single path is postulated to be an exponential whose (imaginary) phase is the classical action (in units of $\hbar$) for the path in question. The total contribution from all paths reaching $x, t$ from the past is the wave function $\psi(x, t)$. This is shown to satisfy Schroedinger's equation. The relation to matrix and operator algebra is discussed. Applications are indicated, in particular to eliminate the coordinates of the field oscillators from the equations of quantum electrodynamics.

## 1. INTRODUCTION

It is a curious historical fact that modern quantum mechanics began with two quite different mathematical formulations: the differential equation of Schroedinger, and the matrix algebra of Heisenberg. The two, apparently dissimilar approaches, were proved to be mathematically equivalent. These two points of view were destined to complement one another and to be ultimately synthesized in Dirac's transformation theory.

This paper will describe what is essentially a third formulation of non-relativistic quantum theory. This formulation was suggested by some of Dirac's[1,2] remarks concerning the relation of classical action[3] to quantum mechanics. A probability amplitude is associated with an entire motion of a particle as a function of time, rather than simply with a position of the particle at a particular time.

The formulation is mathematically equivalent to the more usual formulations. There are, therefore, no fundamentally new results. However, there is a pleasure in recognizing old things from a new point of view. Also, there are problems for which the new point of view offers a distinct advantage. For example, if two systems $A$ and $B$ interact, the coordinates of one of the systems, say $B$, may be eliminated from the equations describing the motion of $A$. The inter-

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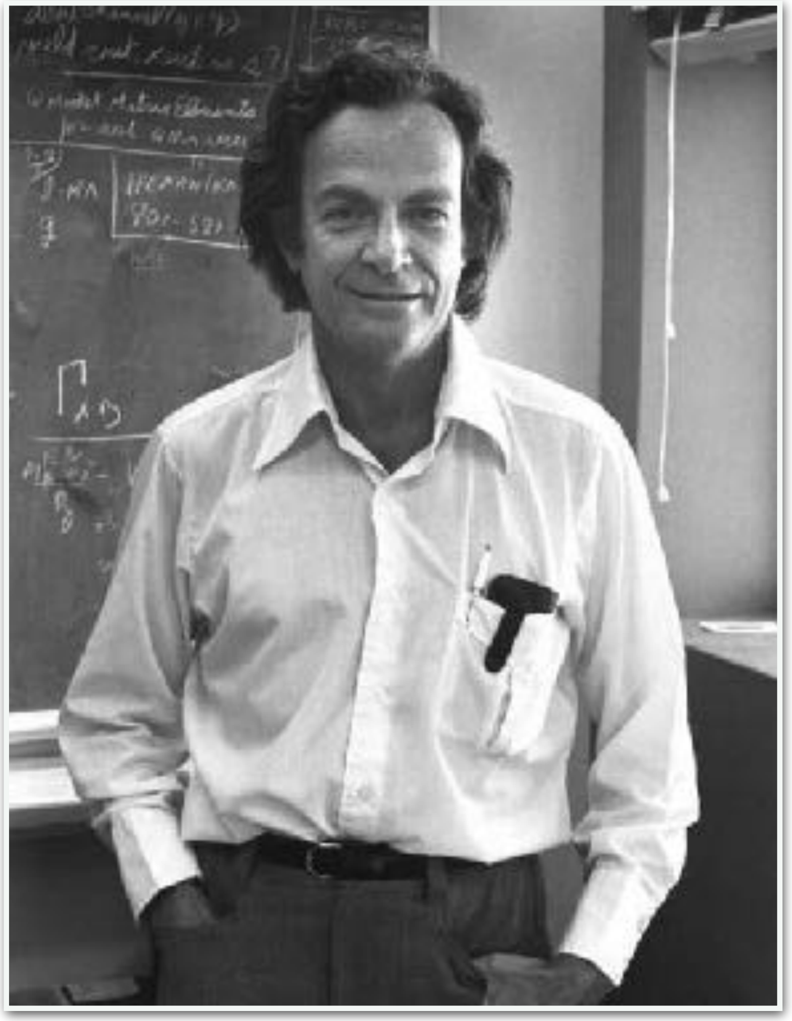
[1] P. A. M. Dirac, *The Principles of Quantum Mechanics* (The Clarendon Press, Oxford, 1935), second edition, Section 33; also, Physik. Zeits. Sowjetunion **3**, 64 (1933).

[2] P. A. M. Dirac, Rev. Mod. Phys. **17**, 195 (1945).

[3] Throughout this paper the term "action" will be used for the time integral of the Lagrangian along a path. When this path is the one actually taken by a particle, moving classically, the integral should more properly be called Hamilton's first principle function.



Richard Phillips Feynman
May 11, 1918 – February 15, 1988
(aged 69)
Nobel Prize in Physics (1965)

# Path integrals

Consider a single particle with Hamiltonian:

$$\hat{H} = \frac{\hat{p}}{2m} + V(\hat{x}) \equiv \hat{K} + \hat{V}$$

What is the amplitude at position x' after time t?

particle is at x at t=0

$$A = \langle x' | e^{-i\hat{H}t/\hbar} | x \rangle \equiv U(x, x', t)$$

*U*: time evolution operator or quantum propagator

Project into coordinate basis:

$$\Psi(x', t) = \langle x' | \Psi(t) \rangle = \int dx \, \langle x' | e^{-i\hat{H}t/\hbar} | x \rangle \Psi(x, 0)$$

needs coordinate-space matrix elements of the propagator

NB: the propagator is connected to the density matrix

# Path integrals in imaginary time

NB: the propagator is connected to the density matrix:

$$\hat{\rho}(\beta) = e^{-\beta \hat{H}}$$

density matrix in the canonical ensemble (N,V,T) -> (1,L,T)

and time operator

$$\hat{U}(t) = e^{-i\hat{H}t/\hbar}$$

inverse temperature: $\beta = \dfrac{1}{k_B T}$

consider the time operator at the imaginary time $t = -i\beta\hbar$

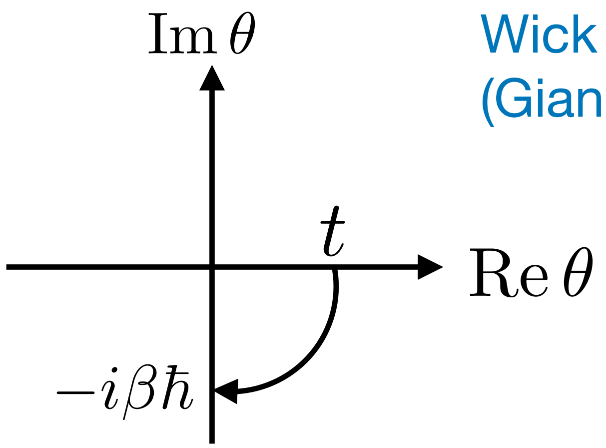
$$\hat{U}(-i\beta\hbar) = e^{-\beta\hat{H}}$$

it gives the density matrix

also consider density operator at the imaginary inverse temperature $\beta = it/\hbar$

$$\hat{\rho}(it/\hbar) = e^{-i\hat{H}t/\hbar}$$

it gives the time operator



Wick rotations (Giancarlo Wick)

Let's define a complex time parameter:

$$\theta = t + i\beta\hbar$$

Transformations are just rotations in the complex plane:

- working in damped exponential is easier than complex exponential…

# Trotter expansion

The coordinate-space matrix elements:

$$\rho(x,x',\beta) \equiv \langle x'|e^{-\beta\hat{H}}|x\rangle = \langle x'|e^{-\beta\hat{K}-\beta\hat{V}}|x\rangle$$

have the problem that the K and V components do not commute.

$$[\hat{K},\hat{V}] \neq 0$$

NB Note analogy with classical Liouville operator expansion…

Use instead a Trotter expansion:

$$e^{-\beta(\hat{K}+\hat{V})} = \lim_{P\to\infty}\left[e^{-\beta\hat{V}/2P}e^{-\beta\hat{K}/P}e^{-\beta\hat{V}/2P}\right]^P$$

Applying P sets of operators to bring the particle from x to x':

$$\rho(x,x',\beta) = \lim_{P\to\infty}\langle x'|\left[e^{-\beta\hat{V}/2P}e^{-\beta\hat{K}/P}e^{-\beta\hat{V}/2P}\right]^P|x\rangle$$

is equivalent to splitting the path into P segments and summing them up:

$$\rho(x,x',\beta) = \lim_{P\to\infty}\sum_{k=1}^{P}\langle x_{k+1}|e^{-\beta\hat{V}/2P}e^{-\beta\hat{K}/P}e^{-\beta\hat{V}/2P}|x_k\rangle$$

(moving through P gratings with holes)

# Trotter expansion

Consider the element: $\langle x_{k+1}|e^{-\beta\hat{V}/2P}e^{-\beta\hat{K}/P}e^{-\beta\hat{V}/2P}|x_k\rangle$

Since V=V(x) a function of positions only, |x> are eigenfunctions of potential operator:

$$= e^{-\beta V(x_{k+1})/2P}\langle x_{k+1}|e^{-\beta\hat{K}/P}|x_k\rangle e^{-\beta V(x_k)/2P}$$

Finding the eigenvalues for the kinetic is less trivial.
Project onto momentum operator using identity: $I = \int dp|p\rangle\langle p|$

$$\langle x_{k+1}|e^{-\beta\hat{K}/P}|x_k\rangle = \int dp\langle x_{k+1}|e^{-\beta\hat{K}/P}|p\rangle\langle p|x_k\rangle$$

$$\langle x_{k+1}|e^{-\beta\hat{K}/P}|x_k\rangle = \int dp\,\langle x_{k+1}||p\rangle\langle p|x_k\rangle e^{-\beta p^2/2mP}$$

$$\langle x_{k+1}|e^{-\beta\hat{K}/P}|x_k\rangle = \frac{1}{2\pi\hbar}\int dp\, e^{-\beta p^2/2mP}e^{ip(x_{k+1}-x_k)/\hbar}$$

Integral over Gaussian

$$\langle x_{k+1}|e^{-\beta\hat{K}/P}|x_k\rangle = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{1/2}\exp\left[-\frac{mP}{2\beta\hbar^2}(x_{k+1}-x_k)^2\right]$$

# Trotter expansion

$$\langle x_{k+1}|e^{-\beta\hat{K}/P}|x_k\rangle = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{1/2}\exp\left[-\frac{mP}{2\beta\hbar^2}(x_{k+1}-x_k)^2\right]$$

combining with potential part and multiplying all P terms in:

$$\rho(x,x',t) = \lim_{P\to\infty}\langle x'|\left[e^{-\beta\hat{V}/2P}e^{-\beta\hat{K}/P}e^{-\beta\hat{V}/2P}\right]^P|x\rangle$$

gives:

$$\rho(x,x',\beta) = \lim_{P\to\infty}\left(\frac{mP}{2m\beta\hbar^2}\right)^{P/2}\int dx_2\dots dx_P$$

integration over all possible paths between x and x' in imaginary time $-i\beta\hbar$

$$\times\exp\left[\frac{1}{\hbar}\sum_{k=1}^{P}\left(\frac{mP}{2\beta\hbar}(x_{k+1}-x_k)^2+\frac{\beta\hbar}{2P}\big(V(x_{k+1})+V(x_k)\big)\right)\right]\Bigg|_{x_1=x}^{x_{P+1}=x'}$$

spring force constant

- quantum kinetic energy is represented by harmonic coupling between nearest neighbours
- the integrant is the amplitude or weight of each discrete path

# Trotter expansion

$$\rho(x,x',\beta) = \lim_{P\to\infty} \left(\frac{mP}{2m\beta\hbar^2}\right)^{P/2} \int dx_2 \dots dx_P$$

$$\times \exp\left[ -\frac{1}{\hbar}\sum_{k=1}^{P}\left(\frac{mP}{2\beta\hbar}(x_{k+1}-x_k)^2 + \frac{\beta\hbar}{2P}\left(V(x_{k+1})+V(x_k)\right)\right)\right]\Bigg|_{x_1=x}^{x_{P+1}=x'}$$

Now the path integral in real time yields:

$$\beta = it/\hbar$$

$$U(x,x',t) = \lim_{P\to\infty} \left(\frac{mP}{2\pi it\hbar}\right)^{P/2} \int dx_2 \dots dx_P$$

$$\times \exp\left[ \frac{i}{\hbar}\sum_{k=1}^{P}\left(\frac{mP}{2t}(x_{k+1}-x_k)^2 - \frac{t}{2P}\left(V(x_{k+1})+V(x_k)\right)\right)\right]\Bigg|_{x_1=x}^{x_{P+1}=x'}$$

note change in sign

# Canonical partition function

$$Q(L,T) = \mathrm{Tr}[\exp(-\beta \hat{H})]$$

trace of density matrix

$$Q(L,T) = \int_0^L dx\, \langle x | e^{-\beta \hat{H}} | x \rangle = \int_0^L dx\, \rho(x,x,\beta)$$

use path integral expression for ρ and set $x_1 = x_{P+1} = x$

paths are confined to the domain [0,L]

$$Q(L,T) = \lim_{P \to \infty} \left( \frac{mP}{2\pi\beta\hbar^2} \right)^{P/2} \int_{D(L)} dx_2 \ldots dx_P$$
$$\times \exp\left[ -\frac{1}{\hbar} \sum_{k=1}^{P} \left( \frac{mP}{2\beta\hbar} (x_{k+1} - x_k)^2 + \frac{\beta\hbar}{P} (V(x_k)) \right) \right] \Bigg|_{x_{P+1}=x_1}$$

potential at position $x_k$

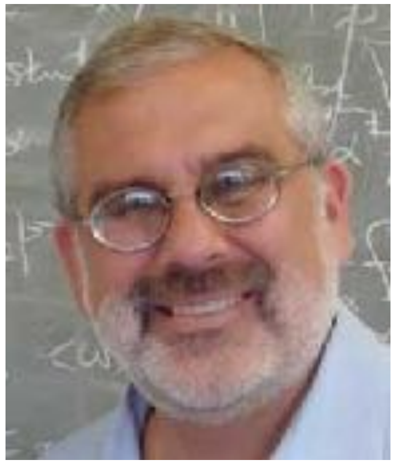
circular paths

at $\beta \to 0$ ($T \to \infty$) the spring constant becomes infinite and the cyclic path collapses onto a single (classical) point.

This expression can be manipulated to resemble the partition function of a cyclic polymer chain moving in a classical potential V(x)/P.

# Path Integral Molecular Dynamics

**David Chandler**



**Peter Wolynes**

“classical isomorphism”
Wolynes and Chandler (1981)

Recast the prefactor as a set of Gaussian integrals of momenta conjugate to $x_k$

$$Q(L,T) = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} \int_{D(L)} dx_1 \dots dx_P \exp\left[-\frac{1}{\hbar}\sum_{k=1}^{P}\left(\frac{mP}{2\beta\hbar}(x_{k+1}-x_k)^2 + \frac{\beta\hbar}{P}(V(x_k))\right)\right]\Bigg|_{x_{P+1}=x_1}$$

finite P (no limit)

$$Q(L,T) = \int dp_1 \dots dp_P \int_{D(L)} dx_1 \dots dx_P$$
$$\times \exp\left[-\beta\sum_{k=1}^{P}\left(\frac{p_k^2}{2m'} + \frac{1}{2}m\omega_P^2(x_{k+1}-x_k)^2 + \frac{1}{P}(V(x_k))\right)\right]\Bigg|_{x_{P+1}=x_1}$$

with nearest-neighbour chain frequency $\omega_P = \sqrt{P}/(\beta\hbar)$

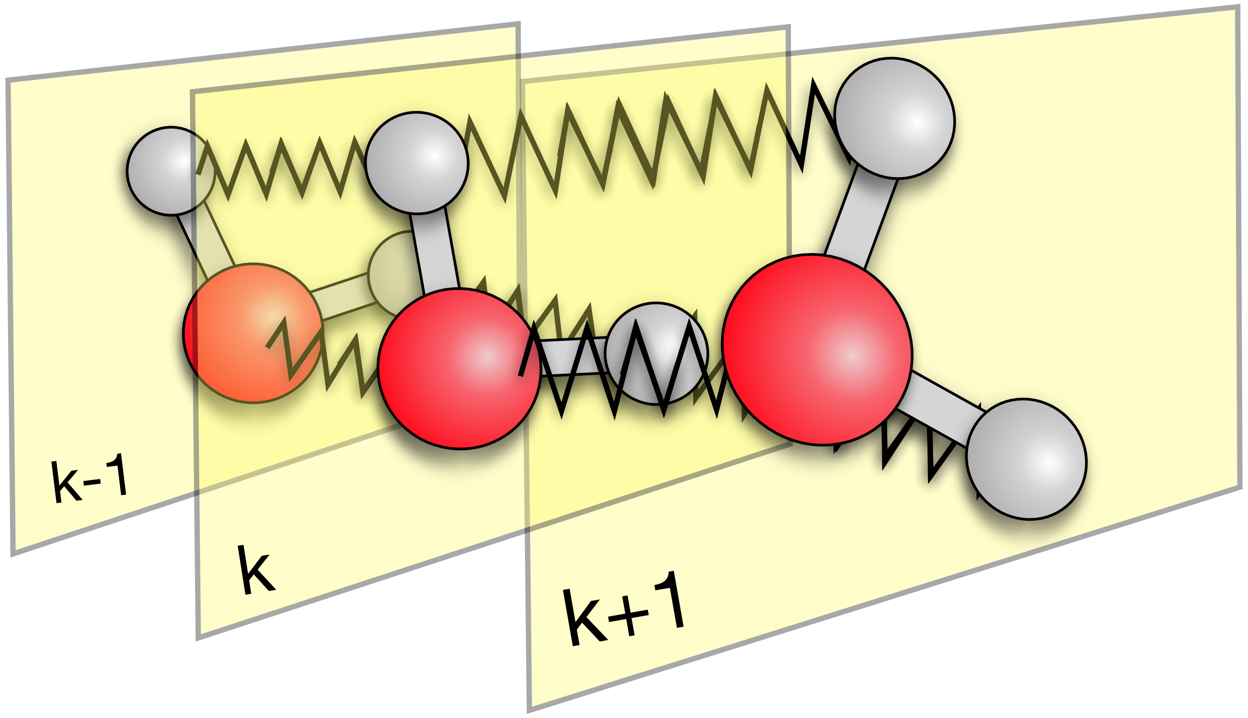
and mass $m' = mP/(2\pi\hbar)^2$

actually prefactor does not affect the distribution, freedom to choose m’

This classical partition function can be sampled by classical MD!
(No quantum dynamics properties (yet)…)

# Path Integral Molecular Dynamics

P replica's of the system

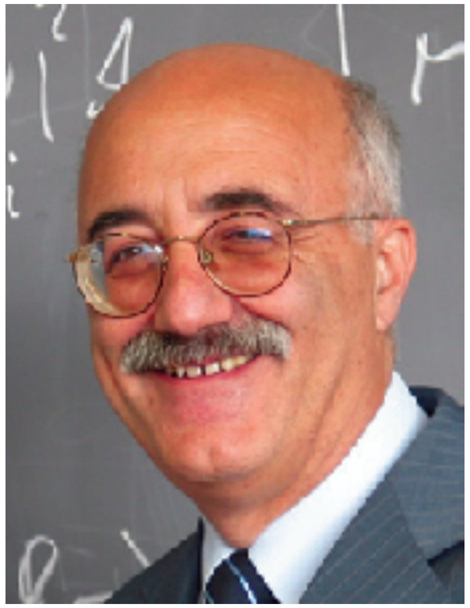


$$Q(L,T) = \int dp_1 \dots dp_P \int_{D(L)} dx_1 \dots dx_P \; \exp[-\beta H(x^P, p^P)]$$

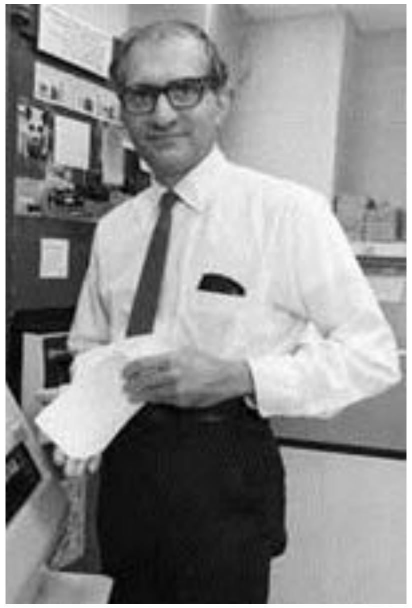
$$\mathcal{H}_{cl}(x,p) = \sum_{k=1}^{P} \left[ \frac{p_k^2}{2m'} + \frac{1}{2} m\omega_P^2 (x_{k+1} - x_k)^2 + \frac{1}{P} U(x_k) \right] \Bigg|_{x_{P+1}=x_1}$$

Equations of motion:

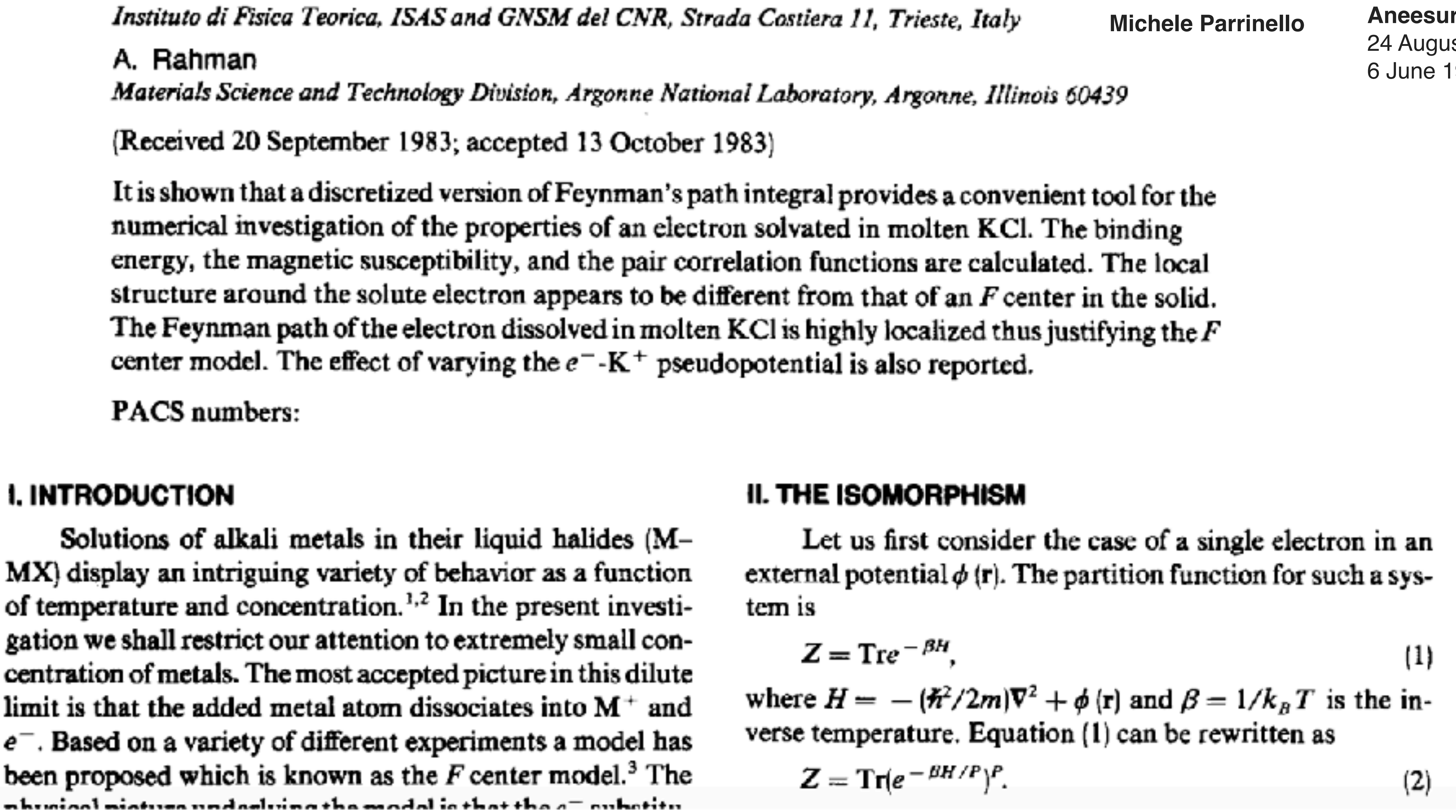
$$\dot{x}_k = \frac{p_k}{m} \qquad \dot{p}_k = -m\omega_P^2 (2x_k - x_{k+1} - x_{k-1}) - \frac{1}{P} \frac{\partial U}{\partial x_k}$$



**Michele Parrinello**



**Aneesur Rahman**
24 August 1927 –
6 June 1987



# Study of an $F$ center in molten KCl[a)]

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It is shown that a discretized version of Feynman's path integral provides a convenient tool for the numerical investigation of the properties of an electron solvated in molten KCl. The binding energy, the magnetic susceptibility, and the pair correlation functions are calculated. The local structure around the solute electron appears to be different from that of an $F$ center in the solid. The Feynman path of the electron dissolved in molten KCl is highly localized thus justifying the $F$ center model. The effect of varying the $e^-$-$K^+$ pseudopotential is also reported.

PACS numbers:

## I. INTRODUCTION

Solutions of alkali metals in their liquid halides (M–MX) display an intriguing variety of behavior as a function of temperature and concentration.[1,2] In the present investigation we shall restrict our attention to extremely small concentration of metals. The most accepted picture in this dilute limit is that the added metal atom dissociates into $M^+$ and $e^-$. Based on a variety of different experiments a model has been proposed which is known as the $F$ center model.[3] The

## II. THE ISOMORPHISM

Let us first consider the case of a single electron in an external potential $\phi(\mathbf{r})$. The partition function for such a system is

$$Z = \mathrm{Tr}\, e^{-\beta H}, \tag{1}$$

where $H = -(\hbar^2/2m)\nabla^2 + \phi(\mathbf{r})$ and $\beta = 1/k_B T$ is the inverse temperature. Equation (1) can be rewritten as

$$Z = \mathrm{Tr}(e^{-\beta H/P})^P. \tag{2}$$

# Path Integral Molecular Dynamics

## Issues with PIMD

- Frequencies of the harmonic normal modes are very high; requires small time step
- Wide range of (continuous) time scales; RESPA multi-time step does not work

## Staging transformation (Tuckerman *et al*. (1993))

- Choose the masses such that only a single harmonic mode remains
- now use RESPA

## Ergodicity (Tuckerman *et al*. (1993))

- massive Nose-Hoover chain thermostat coupled to beads

# Centroid Molecular Dynamics

Cao & Voth (1993)

Based on the centroid density ideas from Feynman & Kleinert (1986))

Evolution of a single centroid particle:

$$\dot{x}_c = \frac{p_c}{m} \qquad \dot{p}_c = \frac{\partial U_0(x_c)}{\partial x_c} \equiv F_o(x_c)$$

physical mass for centroid

with centroid potential of mean force:

cyclic paths with centroid position x$_c$

Euclidian time action

$$U_0(x_c) = -\frac{1}{\beta}\ln\left[\left(\frac{2\pi\beta\hbar^2}{m}\right)^{1/2}\oint \mathcal{D}x(\tau)\delta(x_0[x(\tau)] - x_c)e^{-S[x(\tau)]/\hbar}\right.$$

$$x_0[x(\tau)] = \frac{1}{\beta\hbar}\int dr x(\tau)$$

in PIMD the centroid force is simply obtained from:

$$F_0(x_c) = -\left\langle \frac{1}{P}\sum_{k=1}^{P}\frac{\partial U}{\partial x_k}\delta\left(\frac{1}{P}\sum_{k=1}^{P}x_k - x_c\right)\right\rangle_f$$

note, this still requires a full PI calculation at each centroid configuration.

# Centroid Molecular Dynamics

Cao & Voth (1993)

Adiabatic approximation:

- based on imaginary time PIMD in the normal mode representation
- scale fictitious kinetic masses to accurate the node dynamics

adiabaticity parameter

$$m_{k\neq c} << m_c \qquad m'_k = \gamma^2 m\lambda_k \qquad 0 < \gamma^2 < 1$$

- only non-centroid beads are thermostatted
- assume that Kubo-transformed quantum time correlation function can be approximated by:

$$K_{AB}(t) \approx \frac{1}{Q(\beta)} \int dx_c\, dp_c\, a(x_c(0))b(x_c(t)) \exp\left[-\beta\left(\frac{p_c^2}{2m} + U_0(x_c)\right)\right]$$

CMD is exact in the classic limit and for a purely harmonic potential

# Ring Polymer Molecular Dynamics

Craig & Manolopoulos (2004)

Start from the PIMD EOM:

$$\mathcal{H}_{cl}(x,p) = \sum_{k=1}^{P} \left[ \frac{p_k^2}{2m'} + \frac{1}{2} m\omega_P^2 (x_{k+1} - x_k)^2 + \frac{1}{P} U(x_k) \right] \Bigg|_{x_{P+1}=x_1}$$

$$\dot{x}_k = \frac{p_k}{m} \qquad \dot{p}_k = -m\omega_P^2(2x_k - x_{k+1} - x_{k-1}) - \frac{1}{P}\frac{\partial U}{\partial x_k}$$

to obtain (approximate) real-time dynamics.

- correct in the classical limit and for the harmonic oscillator

$$\mathcal{H}_{cl,P}(x,p) = \sum_{k=1}^{P} \left[ \frac{p_k^2}{2m} + \frac{m}{2\beta_P^2\hbar^2} \sum_{k=1}^{P} (x_k - x_{k+1})^2 + \sum_{k=1}^{P} U(x_k) \right]$$

Newtonial dynamics

$$\dot{x}_k = \frac{p_k}{m} \qquad \dot{p}_k = -\frac{m}{\beta_P^2\hbar^2}(2x_k - x_{k+1} - x_{k-1}) - \frac{\partial U}{\partial x_k}$$

- physical mass is chosen for each bead
- full chain is used to approximate the Kubo-transformed time correlation function
- no massive thermostatting of the beads

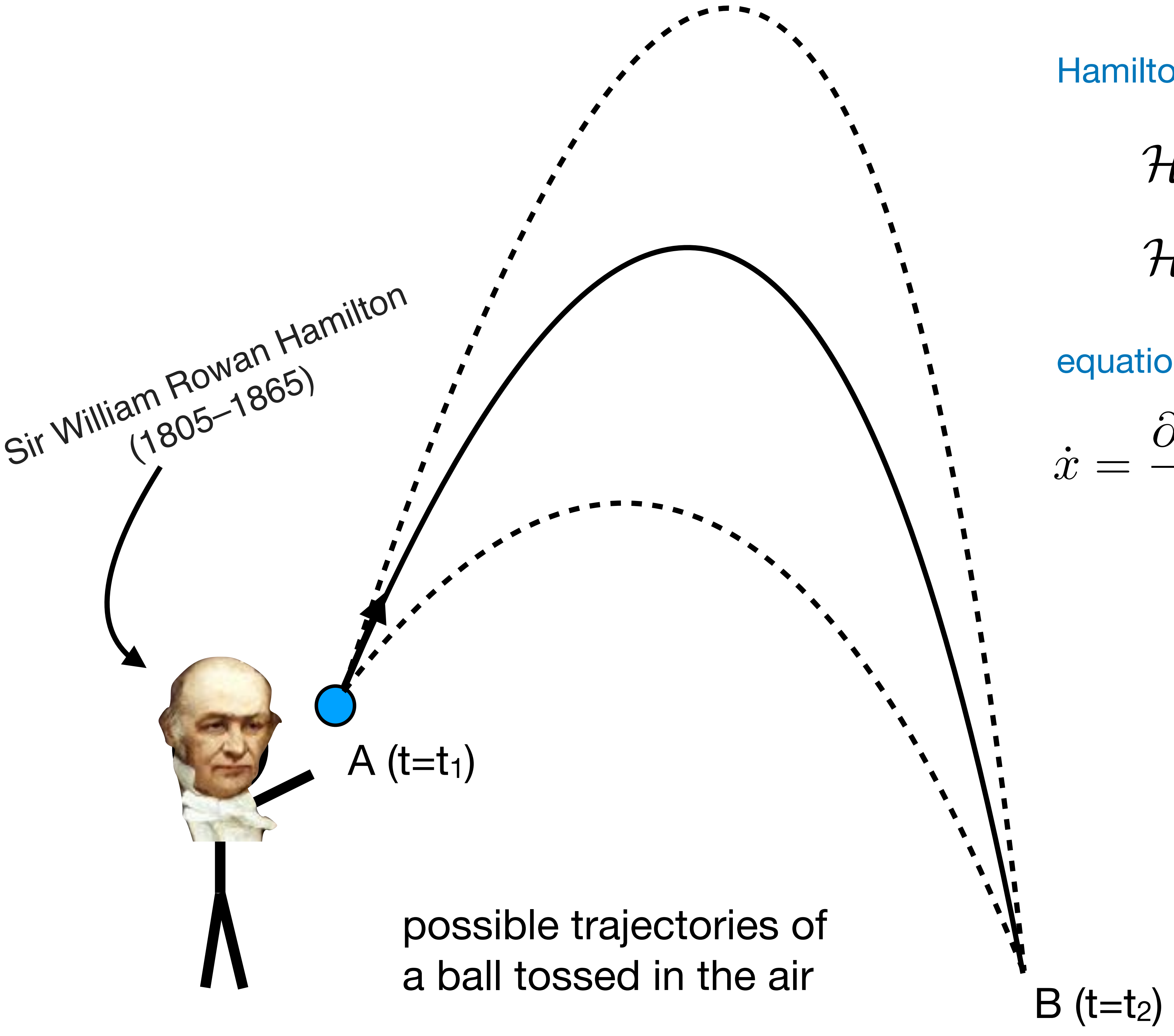
$$A_P(t) = \frac{1}{P}\sum_{k=1}^{P} a(x_k(t))$$

temperature rescaled from T to PT

$$K_{AB}(t) \approx \frac{1}{(2\pi\hbar)^P Q_P(N,V,T)} \int d^P x\, d^P p\, A_P(0) B_P(t) e^{-\beta_P \mathcal{H}_{cl,P}(x,p)}$$

$$\beta_P = \beta/P$$

# Intermezzo: Least action principe



possible trajectories of
a ball tossed in the air

Classical Newtonian dynamics:

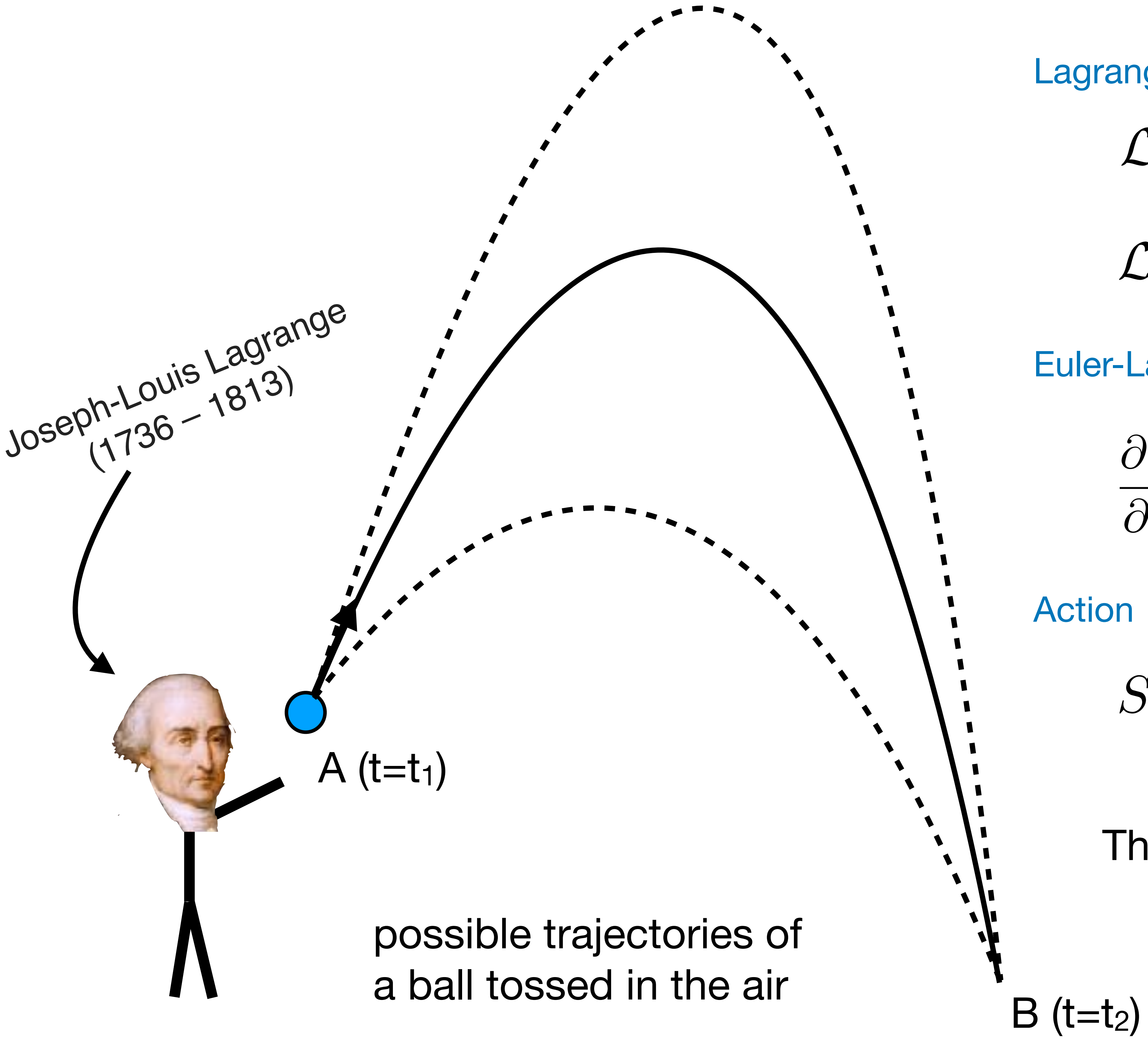
Hamiltonian picture

$$\mathcal{H}(x,p) = K(p) + V(x)$$
$$\mathcal{H}(x,p) = \frac{p^2}{2m} + mgx_z$$

equations of motion

$$\dot{x} = \frac{\partial \mathcal{H}(x,p)}{\partial p} \qquad \dot{p} = -\frac{\partial \mathcal{H}(x,p)}{\partial x}$$

# Intermezzo: Least action principe



possible trajectories of
a ball tossed in the air

Classical Newtonian dynamics:

Lagrangian picture

$$\mathcal{L}(x,p) = K(p) - V(x)$$

$$\mathcal{L}(x,p) = \frac{p^2}{2m} - mgx_z$$

Euler-Lagrange equation

$$\frac{\partial \mathcal{L}}{\partial x} - \frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{x}} + \sum_{i=1}^{C} \lambda_i \frac{\partial f_i}{\partial x} = 0$$

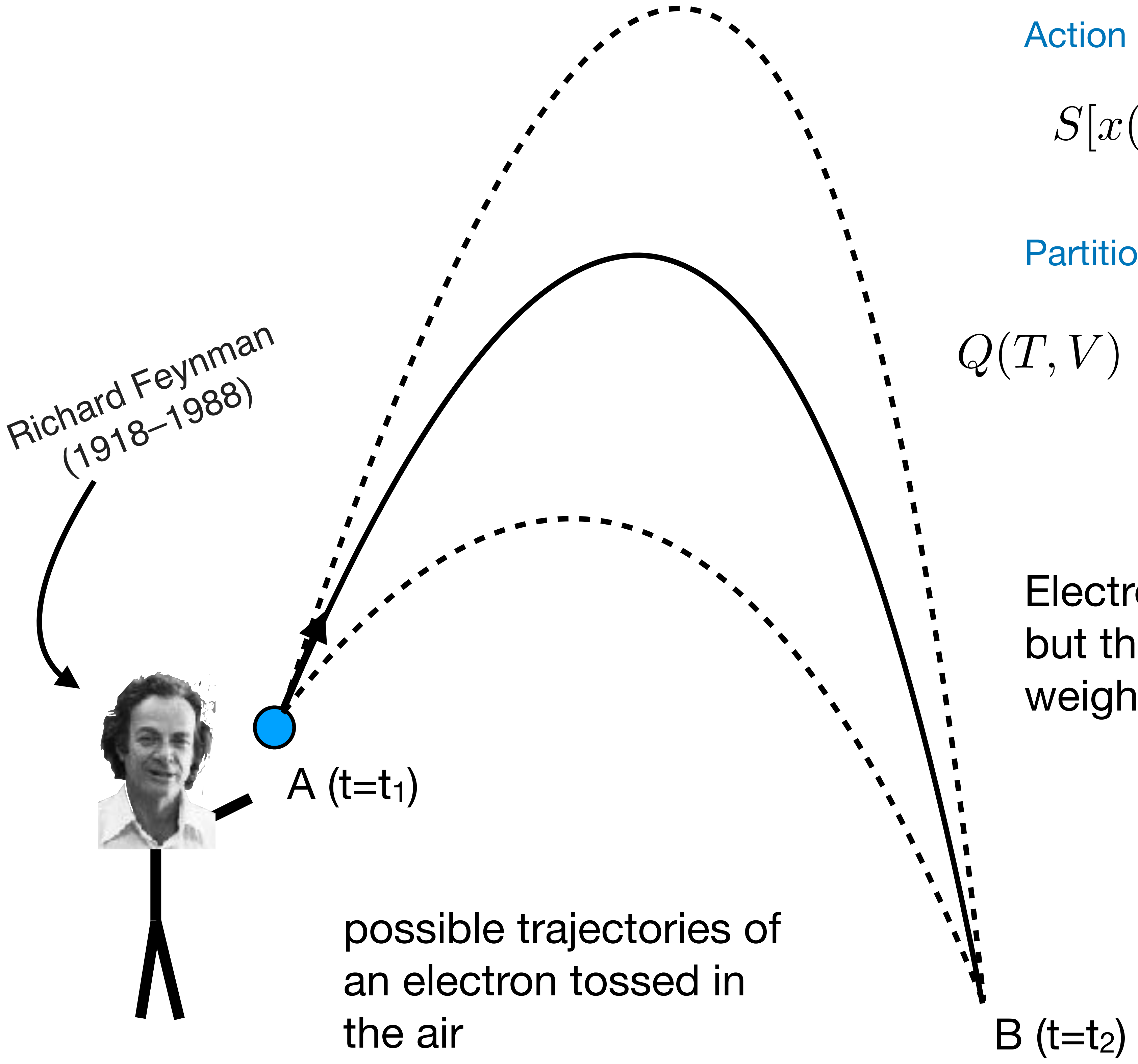
constraints

Action

$$S[\mathcal{L}(t)] = \int_{t_1}^{t_2} \mathcal{L} dt$$

The path of least action is taken.

# Intermezzo: quantum mechanical action principe



possible trajectories of
an electron tossed in
the air

quantum dynamics

Action

$$S[x(\tau)] = \int_0^{\beta\hbar} \mathcal{H}(x(\tau))d\tau$$

Partition function

$$Q(T,V) = \int_V dx \int_{x_1}^{x_2} Dx(\tau) e^{-S[x(\tau)]}$$

integral over paths

Electron takes all possible paths,
but the paths are expontially
weighted by action.

# Time correlation functions, classical

Onsager's regression hypothesis: the macroscopic response of the system to some out-of-equilibrium perturbation follows the same laws as the regression of microscopic fluctuations around the average.

Various transport properties can be calculated from knowledge of time correlation functions, which can be obtained from the system in equilibrium.

Self-diffusion coefficient is related to the velocity auto-correlation:

$$D = \int_0^\infty d\tau \langle v_x(\tau) v_x(0) \rangle$$

Green-Kubo equation

$$\langle x^2(t) \rangle = 2Dt$$

Einstein relation:
mean square displacement
(in 1 dimension)

Thermal conductivity coefficient is related to the heat-flux auto-correlation:

$$\kappa = \frac{V}{k_B T^2} \int_0^\infty \langle J_x(0) J_x(t) \rangle dt$$

$$\mathbf{J} = \frac{1}{V} \left[ \sum_i e_i \mathbf{v}_i + \frac{1}{2} \sum_{i<j} (\mathbf{f}_{ij} \cdot (\mathbf{v}_i + \mathbf{v}_j)) \mathbf{x}_{ij} \right]$$

# Time correlation functions, classical

The Fourier transform of the VACF can be related to the (IR) vibrational spectrum

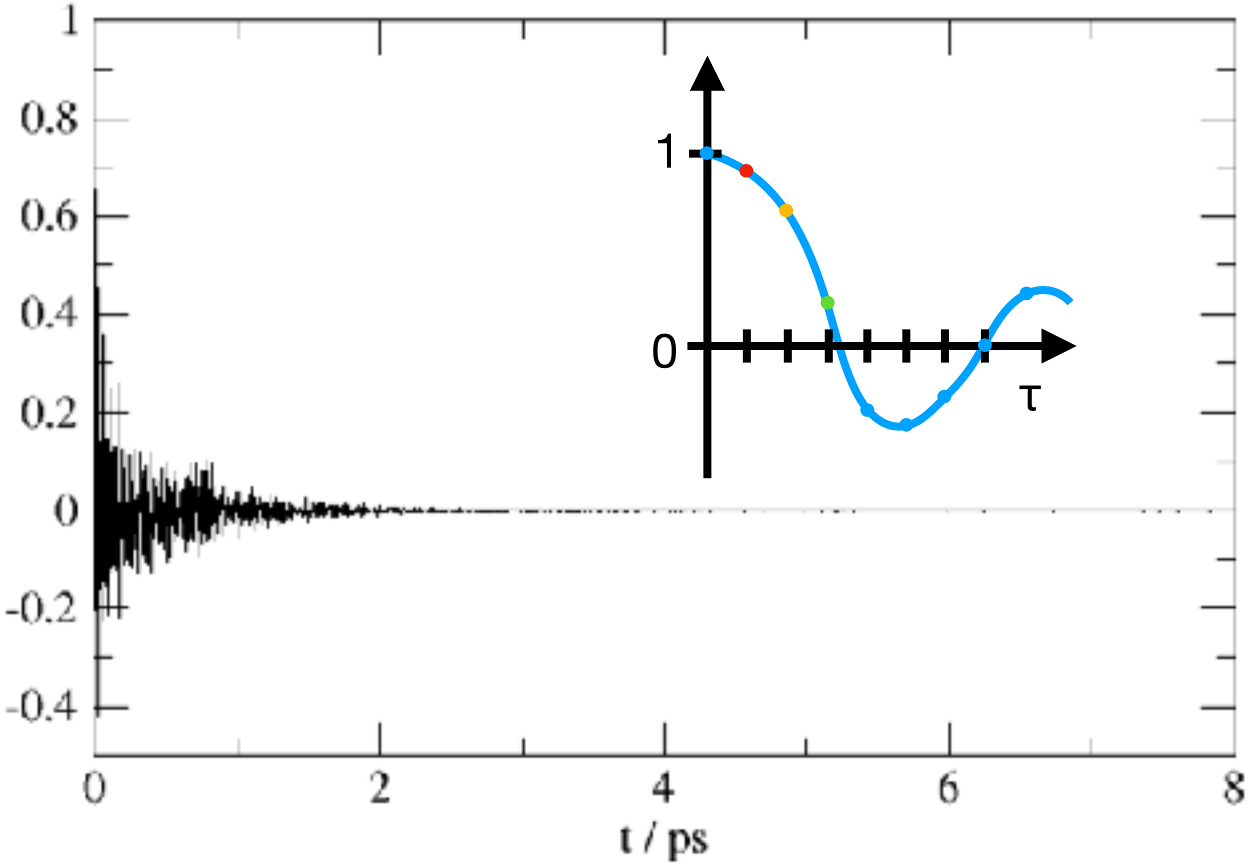
$$c_{vv}(t) = \frac{1}{N}\sum_{i=1}^{N}\sum_{\alpha=1}^{3}\langle v_i^\alpha(0)v_i^\alpha(\tau)\rangle$$

$$C(\omega) = \lim_{\tau\to\infty}\int_{-\tau}^{\tau} c_{vv}(t)e^{-i\omega t}dt$$

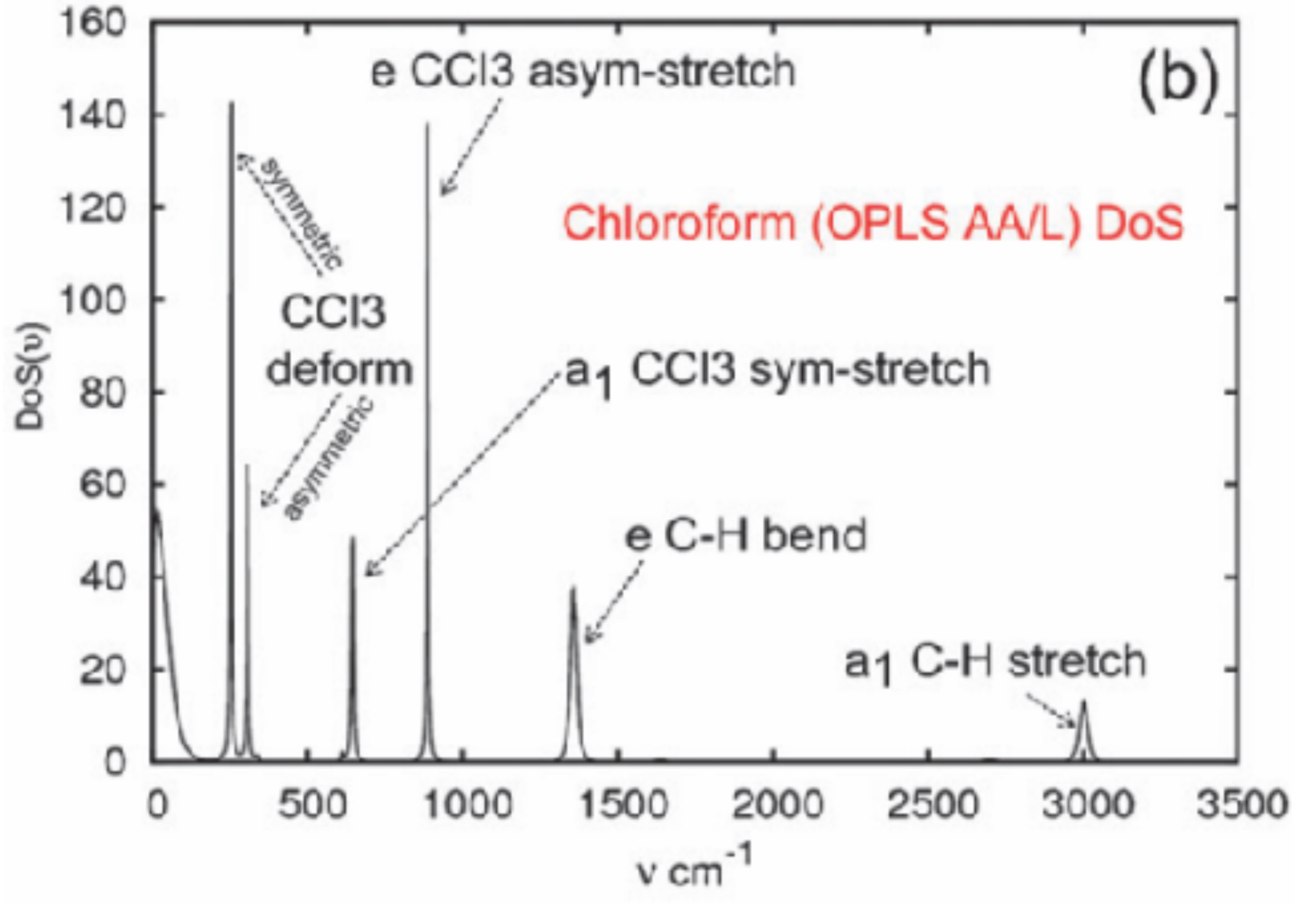
to obtain compatible amplitudes, use the dipole-dipole auto-correlation function

Liquid chloroform

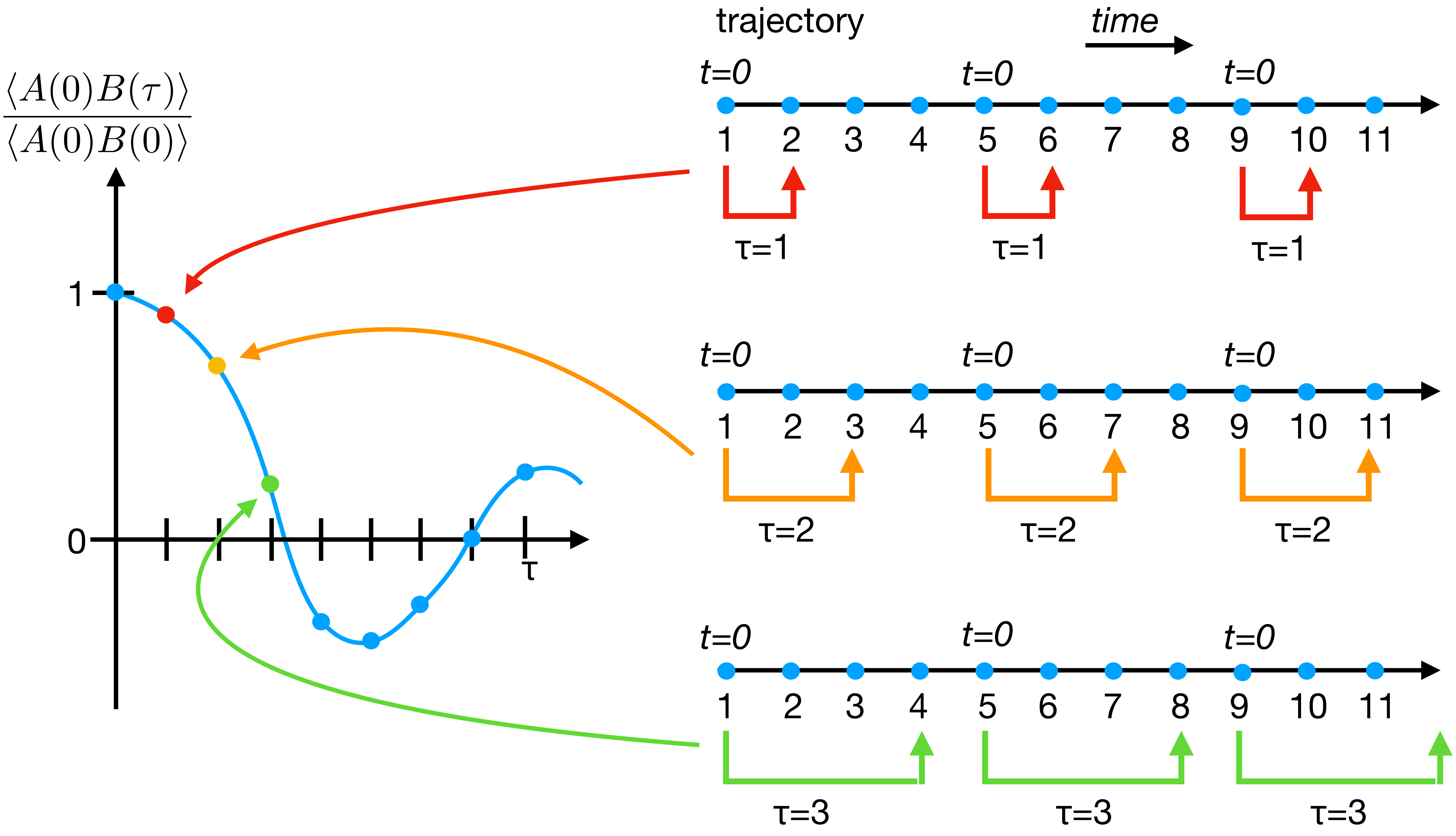
velocity auto-correlation function



IR vibrational spectrum



# Time correlation functions, classical



For implementations see e.g. book “Understanding molecular simulation”, D. Frenkel and B. Smit

# Time correlation functions, quantum mechanical

Classical phase space integral

$$\langle A\rangle = \frac{\iint d\mathbf{r}^N d\mathbf{p}^N A(\mathbf{r}^N,\mathbf{p}^N)\exp[-\beta H(\mathbf{r}^N,\mathbf{p}^N)]}{\iint d\mathbf{r}^N d\mathbf{p}^N \exp[-\beta H(\mathbf{r}^N,\mathbf{p}^N)]}$$

Classical correlation function

omitting the "N" particles

$$c^{cl}_{AB}(t) = Q^{-1}\int dp_0 \int dr_0\, e^{-\beta H(x_0,p_0)} A(x_0,p_0)B(x_t,p_t)$$

This is (also) the classical limit of more one quantum mechanical correlation functions.
Which quantum mechanical correlation function is best approximated by the classical one?

Standard QM analog:

$$c^0_{AB}(t) = Q^{-1}\mathrm{Tr}\left[e^{-\beta\hat{H}}\hat{A}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}\right]$$

But:

- it is a complex valued function of time
- it does not share the detailed balance symmetry

spectral representation:

$$C^0_{AB}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-\omega t} c^0_{AB}(t)$$

$$C^0_{AB}(-\omega) = e^{-\beta\hbar\omega}C^0_{AB}(\omega)$$

$$C^{cl}_{AB}(-\omega) = C^{cl}_{AB}(\omega)$$

# Time correlation functions, the Kubo transform

Standard QM analog:

$$c^{0}_{AB}(t) = Q^{-1}\mathrm{Tr}\left[e^{-\beta\hat{H}}\hat{A}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}\right]$$

Class of QM correlation functions that have the same classical limit:

$$c^{\lambda}_{AB}(t) = Q^{-1}\mathrm{Tr}\left[e^{-(\beta-\lambda)\hat{H}}\hat{A}e^{\lambda\hat{H}}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}\right] \qquad 0 \leq \lambda \leq \beta$$

If $\lambda = \beta/2$, then the QM function shares the same properties as the classical function (real valued, even, detailed balance)

Kubo transform correlation function:

$$c^{\mathrm{kubo}}_{AB}(t) = \frac{1}{\beta}\int_0^{\beta} d\lambda c^{\lambda}_{AB}(t)$$

- Kubo transform can easily be transformed into other QM correlation functions
- Is sampled by PIMD, CMD, RPMD quantum dynamics simulations

J. Chem. Phys. 125, 184507 2006

An accurate and simple quantum model for liquid water

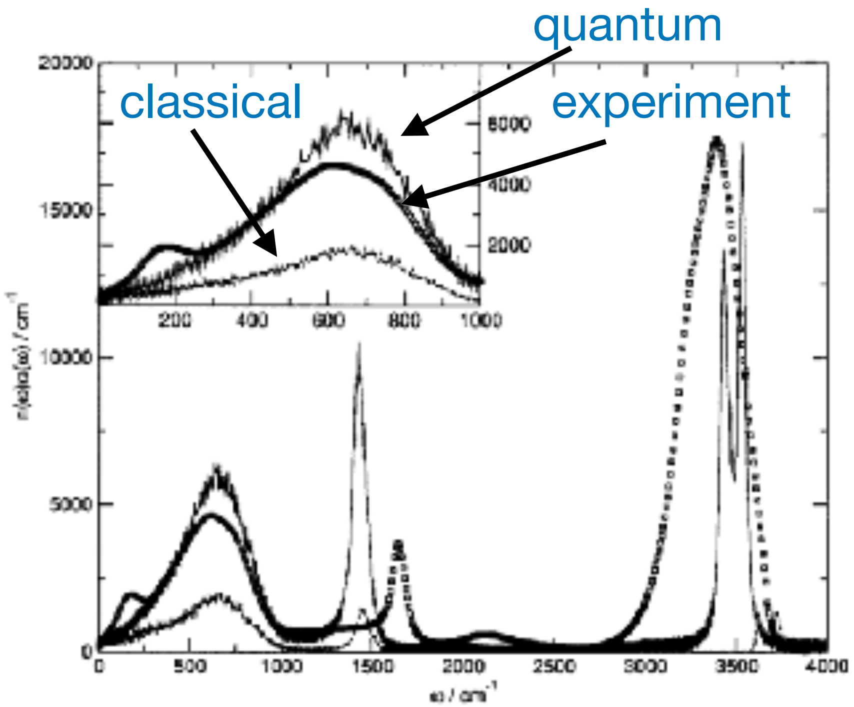
F. Paesani, W. Zhang, D.A. Case, T. E. Cheatham III, G.A. Voth

- simple point charge/flexible SPC/Fw model
- normal-mode path-integral MD
- centroid molecular dynamics

## Conclusions:

“quantum water” is:

- less structured liquid
- reduced amount of hydrogen bonding
- better matching experiment



quantum

classical

experiment

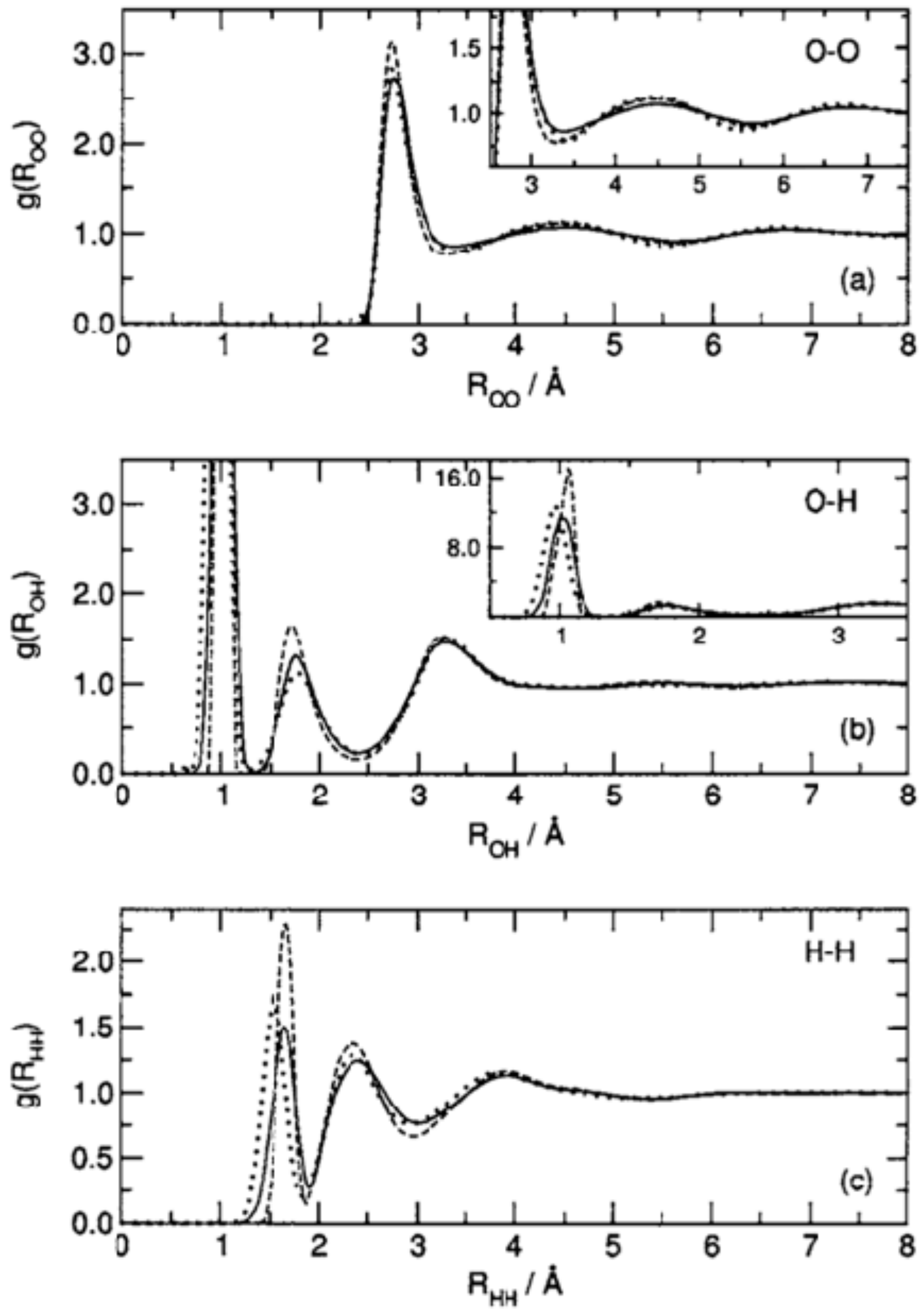


FIG. 1. Radial distribution functions for oxygen-oxygen (a) (the inset is a magnification of the second and third peak), oxygen-hydrogen (b), and hydrogen-hydrogen (c) atom pairs computed with the SPC/Fw water model. Solid line: quantum results from normal-mode path-integral molecular dynamics simulations. Dashed line: results from classical molecular simulations (Ref. 28). Dotted line: experimental data from Ref. 36, panel (a), and from Ref. 35, panels (b) and (c).

# Current developments

- Dynamics, time correlation functions (Ian Craig, David Manolopoulos, et al.)
- Ring contraction / reduction of number of beads (Michele Ceriotti et at, T.Markland, D.E.Manolopoulos et al.)
  - coloured noise Langevin thermosetting of PIMD
  - website: http://gle4md.org/
- Combination with non-adiabatic electron transfer and excited states (Thomas Miller et al)
- i-Pi website: http://ipi-code.org/about/features/
- …

# Summary / take home messages

- Why nuclear quantum dynamics?
  - Zero-point energy and quantum tunnelling are non-negligible for various room-temperature properties (e.g. heat capacity) and processes (e.g. chemical reaction rates)

- Feynman path integral formulation
  - Schrödinger/Heisenberg/Feynman pictures of quantum mechanics
  - double split experiment revisited
  - action principle in quantum mechanics
  - imaginary time <—> inverse temperature
  - isomorphism between quantum distribution and classical ring-polymer

- Practical implementations
  - Centroid molecular dynamics
  - Ring polymer molecular dynamics

- Time correlation functions Application
  - classical, Onsagers regression hypothesis, computing transport properties from equilibrium fluctuations
  - quantum mechanical, which correlation is it?, Kubo transform

- Current/Future developments

# Bibliography / Further reading

- Book: Statistical Mechanics, Theory and Molecular Modelling. Oxford graduate texts. Mark E. Tuckerman
- PhD thesis: Ring polymer molecular dynamics
  Ian R. Craig
  Jesus College, University of Oxford, Hilary term (2006)
- Space-time approach to non-relativistic quantum mechanics
  R.P. Feynman
  *Rev. Mod. Phys.* **20**, 367-387 (1948)
- Quantum Mechanics and Path Integrals,
  R P Feynman and A R Hibbs,
  McGraw-Hill, New York, 1964.
- Exploiting the isomorphism between quantum theory and classical statistical mechanics of polyatomic fluids,
  David Chandler and Peter G Wolynes
  *J. Chem. Phys.* **74**, 4078–4095 (1981)
- Study of an F center in molten KCl,
  M Parrinello and A Rahman
  *J. Chem. Phys.* **80**, 860 (1984)
- On the Simulation of Quantum Systems: Path Integral Methods
  B J Berne and D Thirumalai
  *Annu. Rev. Phys. Chem.* **37**, 401–424, (1986)
- Ab initio path integral molecular dynamics: Basic ideas,
  Dominik Marx and Michele Parrinello
  *J. Chem. Phys.* **104**, 4077 (1996)
- Efficient and general algorithms for path integral Car-Parrinello molecular dynamics
  Mark E Tuckerman, Dominik Marx, Michael L Klein, and Michele Parrinello,
  *J. Chem. Phys.* **104**, 5579–5588 (1996)
- An accurate and simple quantum model for liquid water
  F Paesani, W. Zhang, D.A. Case, T.E. Cheatham, and G.A. Voth
  *J. Chem. Phys.* **125***,* 184507 (2006)
- Competing quantum effects in the dynamics of a flexible water model
  Scott Habershon, Thomas E. Markland, and David E. Manolopoulos
  *J. Chem. Phys.* **131**, 024501 (2009)
- Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory
  Jeremy O. Richardson, and Stuart C. Althorpe
  *J. Chem. Phys.* **131**, 214106 (2009)
- Efficient stochastic thermostatting of path integral molecular dynamics
  Michele Ceriotti, Michele Parrinello, Thomas E. Markland, and David E. Manolopoulos
  *J. Chem. Phys.* **133**, 124104 (2010)
- Accelerating the convergence of path integral dynamics with a generalized Langevin equation
  Michele Ceriotti, David E. Manolopoulos, and Michele Parrinello
  *J. Chem. Phys.* **134**, 084104 (2011)
- Direct simulation of electron transfer using ring polymer molecular dynamics: Comparison with semiclassical instanton theory and exact quantum methods
  Artur R. Menzeleev, Nandini Ananth, and Thomas F. Miller
  *J. Chem. Phys.* **135**, 074106 (2011)
- Can the ring polymer molecular dynamics method be interpreted as real time quantum dynamics?
  Seogjoo Jang, Anton V. Sinitskiy, and Gregory A. Voth
  *J. Chem. Phys.* **140**, 154103 (2014)
- Ab initio molecular dynamics with nuclear quantum effects at classical cost: Ring polymer contraction for density functional theory
  Ondrej Marsalek, and Thomas E. Markland
  *J. Chem. Phys.* **144**, 054112 (2016)
- Ring-Polymer Molecular Dynamics: Quantum Effects in Chemical Dynamics from Classical Trajectories in an Extended Phase Space
  Scott Habershon, David E. Manolopoulos, Thomas E. Markland, and Thomas F. Miller III
  *Annu. Rev. Phys. Chem.* **64,** 387-413. (2013)
- A comparative study of the centroid and ring-polymer molecular dynamics methods for approximating quantum time correlation functions from path integrals.
  A. Perez, M.E. Tuckerman, M.H. Muserå
  *J. Chem. Phys.* **130,** 184105 (2009)