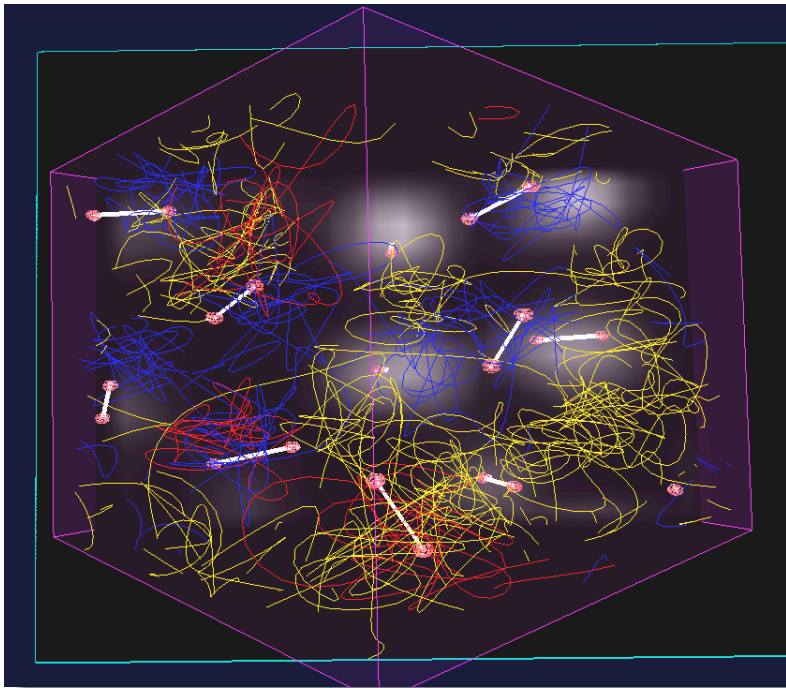# Path Integral Monte Carlo I

Summer school "QMC Theory and Fundamentals"

Burkhard Militzer

University of California, Berkeley

militzer@berkeley.edu

http://militzer.berkeley.edu

Paul Dirac (1929):

The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.

Paul Dirac (1929):

The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved *EXACTLY*.

PIMC: Outline of presentations
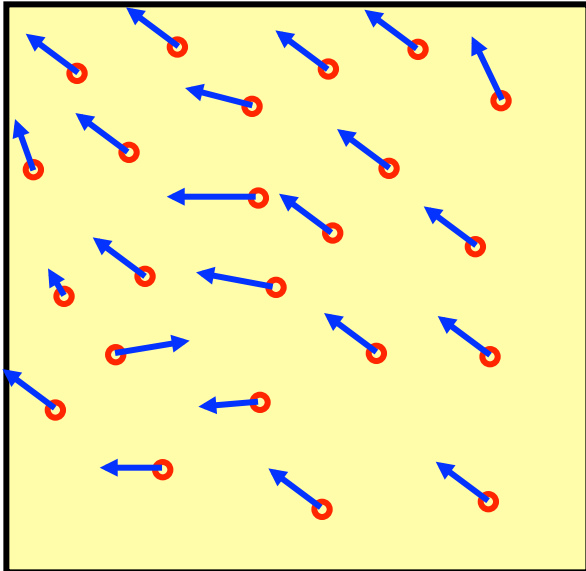
Morning: **Lectures** by BM on:

1: PIMC for distinguishable particles

2: PIMC for bosons

3: PIMC for fermions

Afternoon: **Computer lab** by Kevin Driver and BM on:

– Hydrogen atom and molecule

– Fermions: direct simulations vs. restricted nodes

– **Carbon** plasma: PIMC+DFT

– Hydrogen plasma

Molecular Dynamics (MD)
Simulate the motion of the atoms in real time

Pair potentials:

$$V(R) = \sum_{i>j} V(r_i, r_j)$$

Forces on the atom, Newton's law:

$$F_i = m_i a_i = -\frac{\partial V}{\partial r_i}$$

Change in velocity:

$$\frac{\partial v_i}{\partial t} = \frac{F_i}{m_i}$$

Change in position:

$$\frac{\partial r_i}{\partial t} = v_i$$

Microcanonical ensemble: Total energy is constant: **E=K+V** but **K** and **V** fluctuate:
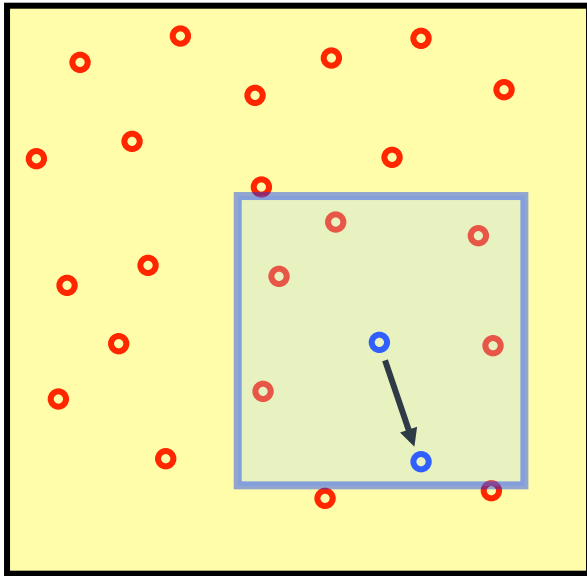
$$\langle K \rangle = \sum \tfrac{1}{2} \, m \, \langle \vec{v}^2 \rangle = \tfrac{3}{2} N \, k_b T \qquad \langle V \rangle = \left\langle \sum_{i>j} V(r_i, r_j) \right\rangle$$

Real time dynamics: Can e.g. determine the diffusion constant or watch proteins fold.

Monte Carlo (MC)
Generate states in the microcanonical ensemble

Metropolis algorithm (1953):

1. Start from configuration R_{old}
2. Propose a random move $R_{old} \rightarrow R_{new}$
3. Compute energies $E_{old}=V(R_{old})$ and $E_{new}=V(R_{new})$
4. If $E_{new}<E_{old}$ (down-hill) $\rightarrow$ always accept.
5. If $E_{new}>E_{old}$ (up-hill) $\rightarrow$ accept with probability

$$A(R_{old} \rightarrow R_{new}) = \exp\left[-\frac{V(R_{new})-V(R_{old})}{k_b T} \right]$$

Generate a Markov chain of configurations: R_1, R_2, R_3, ...

$$\langle O \rangle = \frac{\int dR\, O(R)\, e^{-\beta V(R)}}{\int dR\, e^{-\beta V(R)}} = \frac{1}{N}\sum_{i=1}^{N} O(R_i)$$

The Boltzmann factor is absorbed into the generated ensemble.
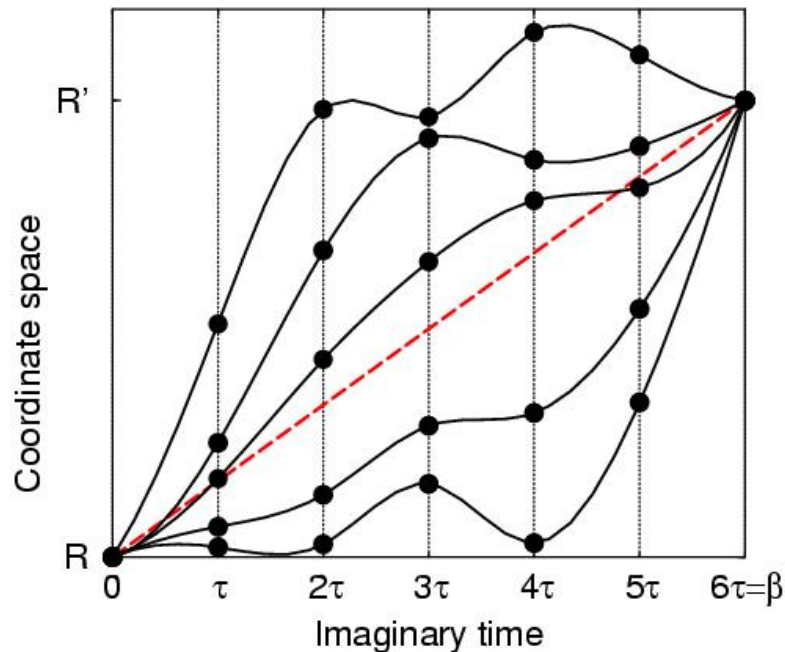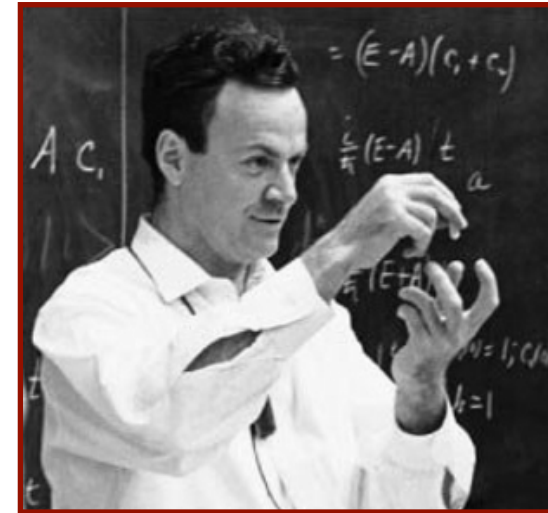
I. Path Integral Fundamentals

Quantum systems at finite temperature:
Richard Feynman's path integrals

Real time path integrals
(not practical for simulations because oscillating phase)

$$\Psi(R,t) = \int dR' \; G(R,R',t-t') \; \Psi(R',t')$$

$$\Psi(R,t) = \int dR' \; e^{-i(t-t')\,\hat{H}} \; \Psi(R',t')$$

Imaginary time path integrals $\tau=it$
(used for many simulations at T=0 and T>0)

$$f(R,\tau) = \int dR' \; e^{-(\tau-\tau')\,\hat{H}} \; f(R',\tau')$$

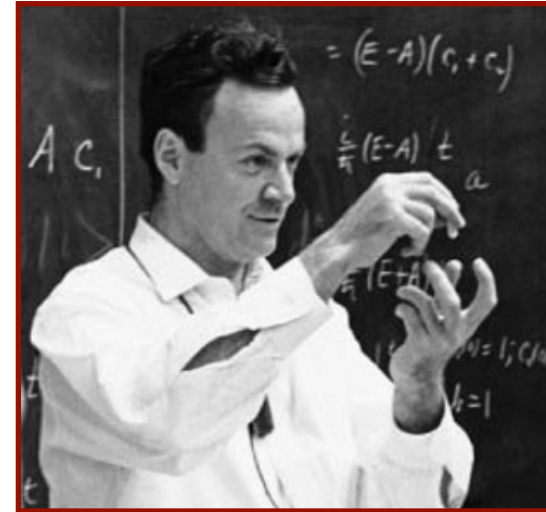$$\rho(R,R',\beta) = \langle R | e^{-\beta\,\hat{H}} | R' \rangle$$

$$e^{-\beta\,\hat{H}} = e^{-E/k_B T}$$

The principal object in PIMC: Thermal density matrix $\rho(R,R';\beta)$

Density matrix definition:

$$\rho(R,R',\beta) = \left\langle R \left| e^{-\beta \hat{H}} \right| R' \right\rangle$$

$$\rho(R,R',\beta) = \sum_S e^{-\beta E_S} \Psi_S^*(R) \Psi_S(R')$$

Density matrix properties:

$$Tr[\hat{\rho}] = \int dR \left\langle R \left| e^{-\beta \hat{H}} \right| R \right\rangle$$

$$\left\langle \hat{O} \right\rangle = \frac{Tr[\hat{O} \hat{\rho}]}{Tr[\hat{\rho}]}$$

Imaginary time path integrals $\tau=it$

(used for many simulations)

$$f(R,\tau) = \int dR' \; e^{-(\tau-\tau') \hat{H}} f(R',\tau')$$

$$\rho(R,R',\beta) = \left\langle R \left| e^{-\beta \hat{H}} \right| R' \right\rangle$$
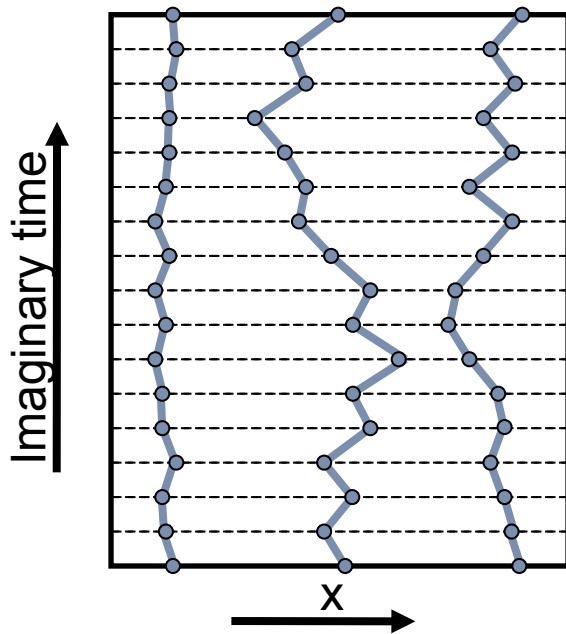
$$e^{-\beta \hat{H}} = e^{-E \;/\; k_B T}$$

The principal object in PIMC:
Thermal density matrix $\rho(R,R';\beta)$

Density matrix definition:

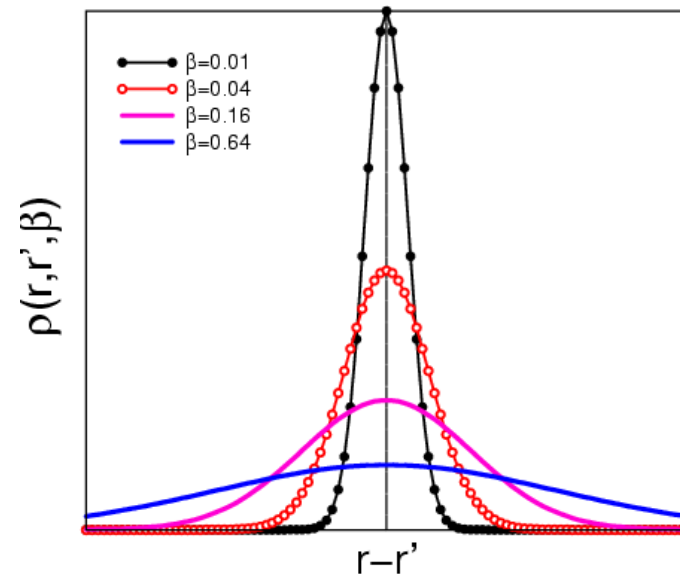$$\rho(R,R',\beta) = \langle R | e^{-\beta \hat{H}} | R' \rangle$$

$$\rho(R,R',\beta) = \sum_S e^{-\beta E_S} \Psi_S^*(R) \, \Psi_S(R')$$

Imaginary time

x

Free particle density matrix:

$$\rho(r,r',\beta) = \frac{1}{V} \int d^3k \; e^{-\beta\lambda k^2} \; e^{-ikr} e^{+ikr'}$$

$$\rho(r,r',\beta) = (4\pi\lambda\beta)^{-D/2} \; \exp\left[-\frac{(r-r')^2}{4\lambda\beta} \right]$$

- $\beta=0.01$
- $\beta=0.04$
- $\beta=0.16$
- $\beta=0.64$

$\rho(r,r',\beta)$

$r-r'$

$$\lambda = \frac{\hbar^2}{2m}$$

$$\beta = \frac{1}{k_b T}$$

Step 1 towards the path integral
Matrix squaring property of the density matrix

Matrix squaring in operator notation:

$$\hat{\rho} = e^{-\beta\hat{H}} = \left(e^{-(\beta/2)\hat{H}}\right)\left(e^{-(\beta/2)\hat{H}}\right), \quad \beta = \frac{1}{k_B T}$$

Matrix squaring in real-space notation:

$$\langle R | \hat{\rho} | R' \rangle = \int dR_1 \, \langle R | e^{-(\beta/2)\hat{H}} | R_1 \rangle \, \langle R_1 | e^{-(\beta/2)\hat{H}} | R' \rangle$$

Matrix squaring in matrix notation:

$$\begin{bmatrix} \cdots & R' & \cdots \\ R & \ddots & \vdots \\ \cdots & \cdots & \cdots \end{bmatrix} = \begin{bmatrix} \cdots & R_1 & \cdots \\ R & \ddots & \vdots \\ \cdots & \cdots & \cdots \end{bmatrix} * \begin{bmatrix} \cdots & R' & \cdots \\ R_1 & \ddots & \vdots \\ \cdots & \cdots & \cdots \end{bmatrix}$$

Repeat the matrix squaring step

Matrix squaring in operator notation:

$$\hat{\rho} = e^{-\beta\hat{H}} = \left(e^{-(\beta/4)\hat{H}} \right)^4 , \quad \beta = \frac{1}{k_B T}$$

Matrix squaring in real-space notation:

$$\langle R | \hat{\rho} | R' \rangle = \int dR_1 \int dR_2 \int dR_3 \langle R | e^{-(\beta/4)\hat{H}} | R_1 \rangle \langle R_1 | e^{-(\beta/4)\hat{H}} | R_2 \rangle \langle R_2 | e^{-(\beta/4)\hat{H}} | R_3 \rangle \langle R_3 | e^{-(\beta/4)\hat{H}} | R' \rangle$$

Path Integrals in Imaginary Time

Every particle is represented by a path, a ring polymer.

Density matrix:

$$\hat{\rho} = e^{-\beta \hat{H}} = \left(e^{-\tau \hat{H}} \right)^{M} , \quad \beta = \frac{1}{k_B T} , \quad \tau = \frac{\beta}{M}$$

$$\langle \hat{O} \rangle = \frac{\mathrm{Tr}[\hat{O}\hat{\rho}]}{\mathrm{Tr}[\hat{\rho}]}$$
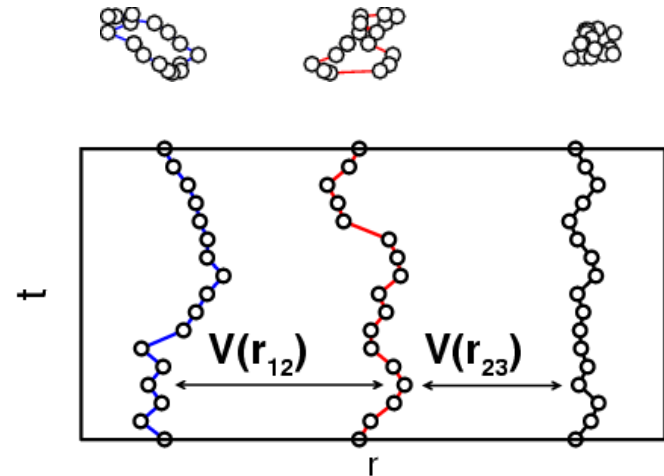
Trotter break-up:

$$\langle R | \hat{\rho} | R' \rangle = \langle R | (e^{-\tau \hat{H}})^{M} | R' \rangle = \int dR_1 ... \int dR_{M-1} \langle R | e^{-\tau \hat{H}} | R_1 \rangle \langle R_1 | e^{-\tau \hat{H}} | R_2 \rangle ... \langle R_{M-1} | e^{-\tau \hat{H}} | R' \rangle$$

Path Integrals in Imaginary Time

Mathematical basis: Trotter formula

Density matrix: $\hat{\rho} = e^{-\beta\hat{H}} = \left(e^{-\tau\hat{H}}\right)^{M}, \ \beta = \dfrac{1}{k_B T}, \ \tau = \dfrac{\beta}{M}$ $\qquad \langle\hat{O}\rangle = \dfrac{\text{Tr}[\hat{O}\hat{\rho}]}{\text{Tr}[\hat{\rho}]}$

Trotter break-up:

$$\langle R\,|\,\hat{\rho}\,|\,R'\rangle = \langle R\,|\,(e^{-\tau\hat{H}})^{M}\,|\,R'\rangle = \int dR_1...\int dR_{M-1}\langle R\,|\,e^{-\tau\hat{H}}\,|\,R_1\rangle\langle R_1\,|\,e^{-\tau\hat{H}}\,|\,R_2\rangle...\langle R_{M-1}\,|\,e^{-\tau\hat{H}}\,|\,R'\rangle$$

Trotter formula:

$$e^{-\beta(\hat{T}+\hat{V})} = \lim_{M\to\infty}\left[e^{-\tau\,\hat{T}}e^{-\tau\,\hat{V}}\right]^{M}$$

Path Integrals in Imaginary Time
Simplest form for the paths' action: primitive approx.

Density matrix:

$$\hat{\rho} = e^{-\beta\hat{H}} = \left(e^{-\tau\hat{H}}\right)^M, \quad \beta = \frac{1}{k_B T}, \quad \tau = \frac{\beta}{M}$$

$$\langle\hat{O}\rangle = \frac{\text{Tr}[\hat{O}\hat{\rho}]}{\text{Tr}[\hat{\rho}]}$$

Trotter break-up:

$$\langle R|\hat{\rho}|R'\rangle = \langle R|(e^{-\tau\hat{H}})^M|R'\rangle = \int dR_1 ... \int dR_{M-1}\langle R|e^{-\tau\hat{H}}|R_1\rangle\langle R_1|e^{-\tau\hat{H}}|R_2\rangle...\langle R_{M-1}|e^{-\tau\hat{H}}|R'\rangle$$

Trotter formula:

$$e^{-\beta(\hat{T}+\hat{V})} = \lim_{M\to\infty}\left[e^{-\tau\hat{T}}e^{-\tau\hat{V}}\right]^M$$

Path integral and primitive action S :

$$\langle R|\hat{\rho}|R'\rangle = \oint_{R\to R'} dR_t e^{-S[R_t]}$$

$$S[R_t] = \sum_{i=1}^{M}\frac{(R_{i+1}-R_i)^2}{4\lambda\tau} + \frac{\tau}{2}\left[V(R_i)+V(R_{i+1})\right]$$

Path Integrals in Imaginary Time
Every particle is represented by a path, a ring polymer.

Density matrix:

$$\hat{\rho} = e^{-\beta\hat{H}} = \left(e^{-\tau\hat{H}}\right)^M, \quad \beta = \frac{1}{k_B T}, \quad \tau = \frac{\beta}{M}$$

$$\langle\hat{O}\rangle = \frac{\text{Tr}[\hat{O}\hat{\rho}]}{\text{Tr}[\hat{\rho}]}$$

Trotter break-up:

$$\langle R\,|\,\hat{\rho}\,|\,R'\rangle = \langle R\,|\,(e^{-\tau\hat{H}})^M\,|\,R'\rangle = \int dR_1 ... \int dR_{M-1}\langle R\,|\,e^{-\tau\hat{H}}\,|\,R_1\rangle\langle R_1\,|\,e^{-\tau\hat{H}}\,|\,R_2\rangle ... \langle R_{M-1}\,|\,e^{-\tau\hat{H}}\,|\,R'\rangle$$

Analogy to groundstate QMC:

$$\Psi_0(R) = \lim_{M\to\infty} (e^{-\tau\hat{H}})^M\,|\,\Psi_T\rangle = \int dR_1 ... \int dR_{M-1}\langle R\,|\,e^{-\tau\hat{H}}\,|\,R_1\rangle\langle R_1\,|\,e^{-\tau\hat{H}}\,|\,R_2\rangle ... \langle R_{M-1}\,|\,e^{-\tau\hat{H}}\,|\,\Psi_T\rangle$$

PIMC literature:

D. Ceperley, *Rev. Mod. Phys.* **67** (1995) 279.

R. Feynman, "Statistical Mechanics", Addison-Wesley, 1972.

B. Militzer, PhD thesis, see http://militzer.berkeley.edu

Temperature and Mass determine the range of diffusion in imaginary time

Imaginary time

Thermal de Broglie wavelength

$$\Lambda = \sqrt{4\pi\lambda\beta}$$

$$\Lambda = \sqrt{2\pi\hbar^2/mk_bT}$$

x

Temperature and Mass determine the range of diffusion in imaginary time

Imaginary time

x
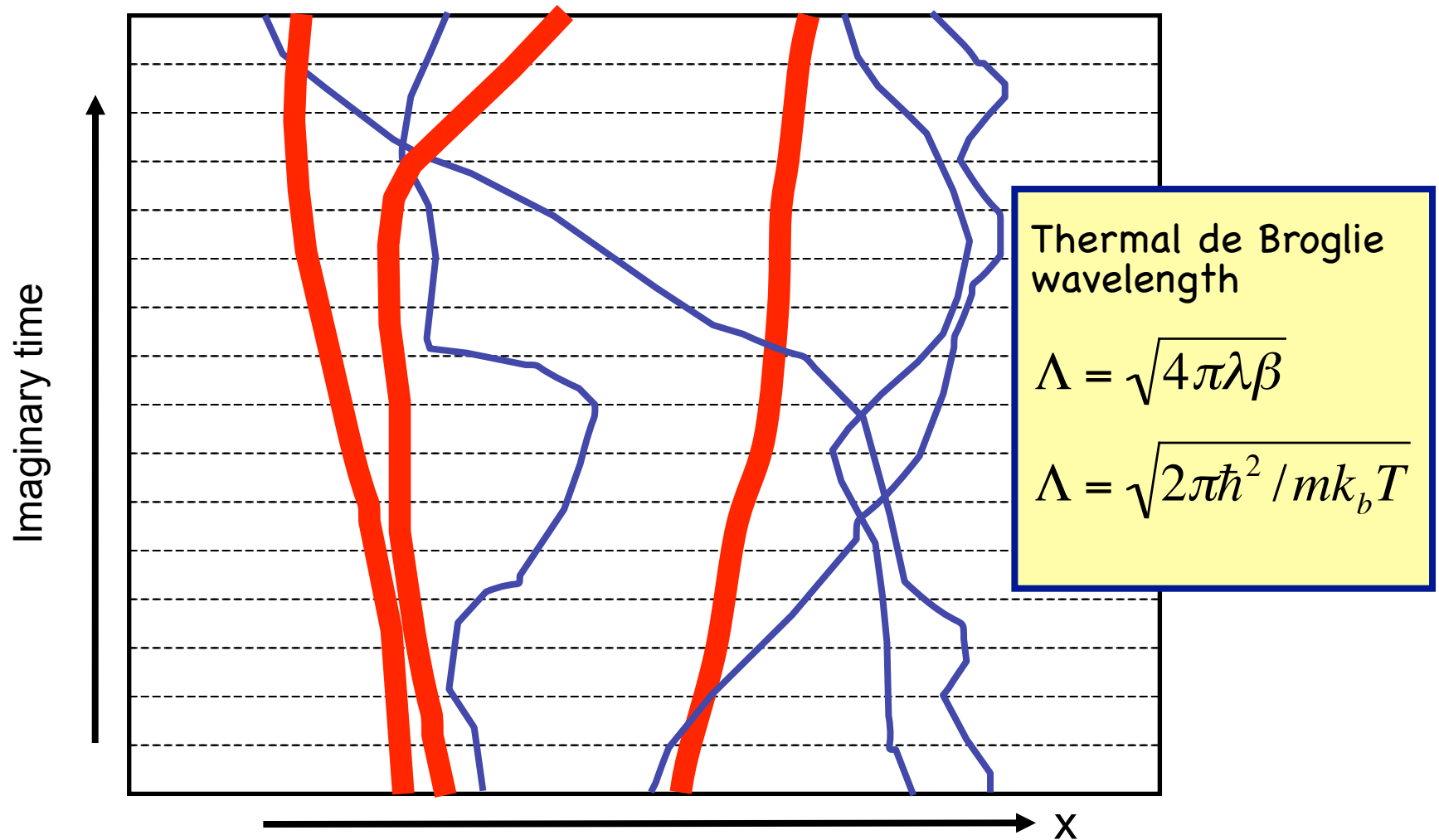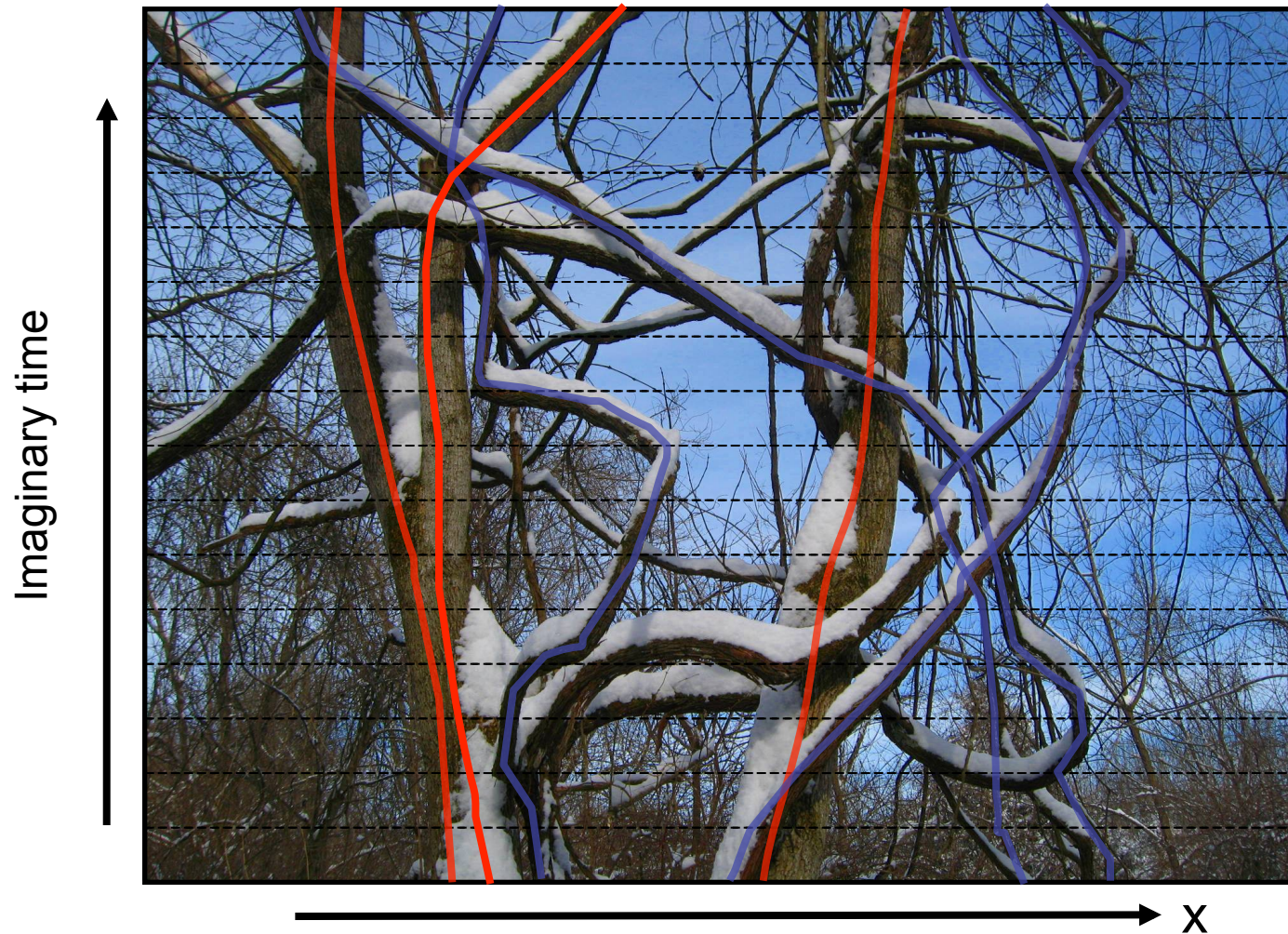
II. Write your own PIMC code

Write your own PIMC code
What is needed to start?
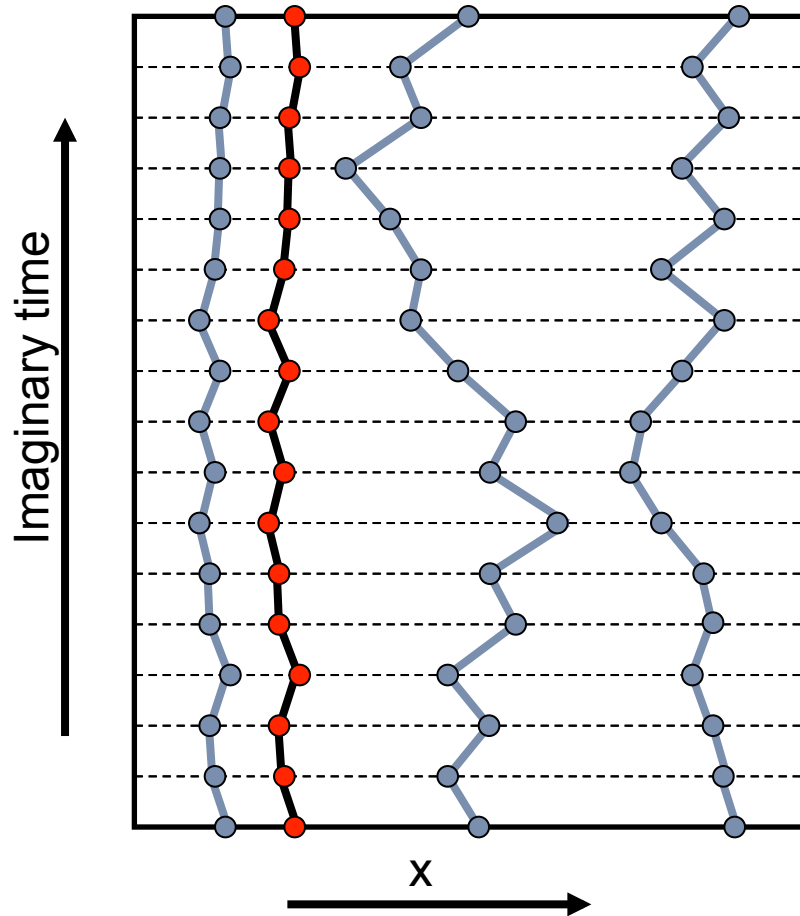
1) Initialize the paths as classical particle on a lattice.
2) Pick one "bead" and sample new position
3) Compute the difference in *kinetic and potential action*
4) Accept or reject based on

$$A(R_{old} \rightarrow R_{new}) = \min\left\{1, \frac{\exp[-S(R_{new})]}{\exp[-S(R_{old})]}\right\}$$

5) Try a "classical" move – shift a polymer as a whole.
6) Compute *potential action* and accept or reject.
7) Go back to step 2).

Example: PIMC for the harmonic oscillator

Classical simulation for
T→0
Gives the classical
ground state E_0=0

$E_3 = \frac{7}{2}\hbar\omega$

$E_2 = \frac{5}{2}\hbar\omega$

$E_1 = \frac{3}{2}\hbar\omega$
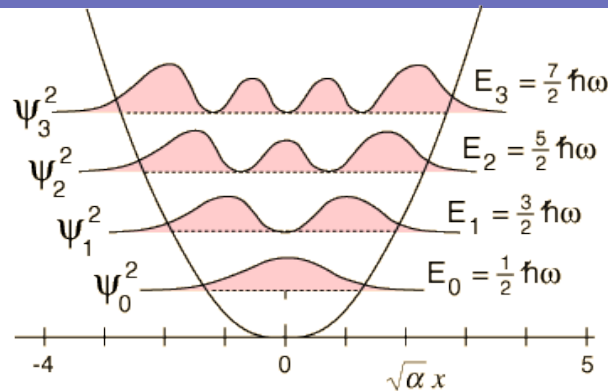
$E_0 = \frac{1}{2}\hbar\omega$

PIMC simulation for
T→0 give the correct
qm groundstate energy

$$E_0 = \frac{1}{2}\hbar\omega$$
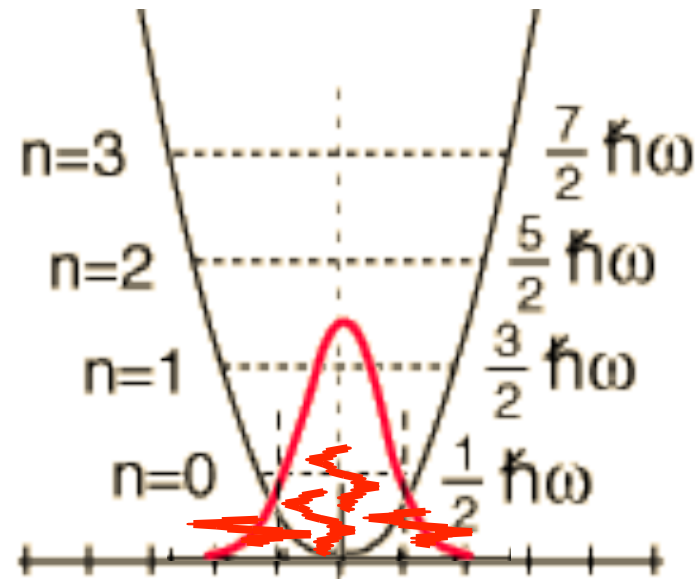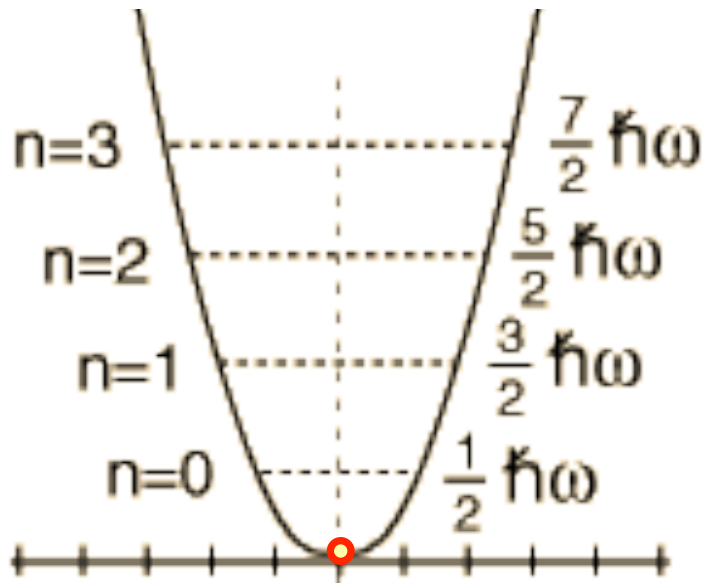
Observables: How do we compute the kinetic and potential energy

Remember the primitive action:

$$\langle R \mid \hat{\rho} \mid R' \rangle = \oint_{R \to R'} dR_t \, e^{-S[R_t]}$$

$$S[R_t] = \sum_{i=1}^{M} \frac{(R_{i+1} - R_i)^2}{4\lambda\tau} + \frac{\tau}{2}\left[V(R_i) + V(R_{i+1})\right]$$
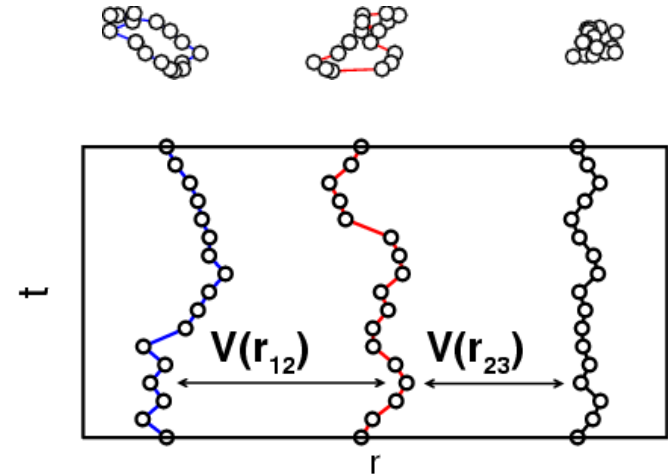
Estimator for kinetic energy:

$$\langle K \rangle = \frac{3N}{2}\log(4\pi\lambda\tau) + \frac{(R_{i+1} - R_i)^2}{4\lambda\tau}$$

(Quantum particle do not longer a kinetic energy of 3/2 k_BT)

Estimator for potential energy:

$$\langle V \rangle = \frac{\tau}{2}\left[V(R_i) + V(R_{i+1})\right]$$

III. Sampling the paths efficiently

Much better efficiency through direct sampling of the free particle d.m.
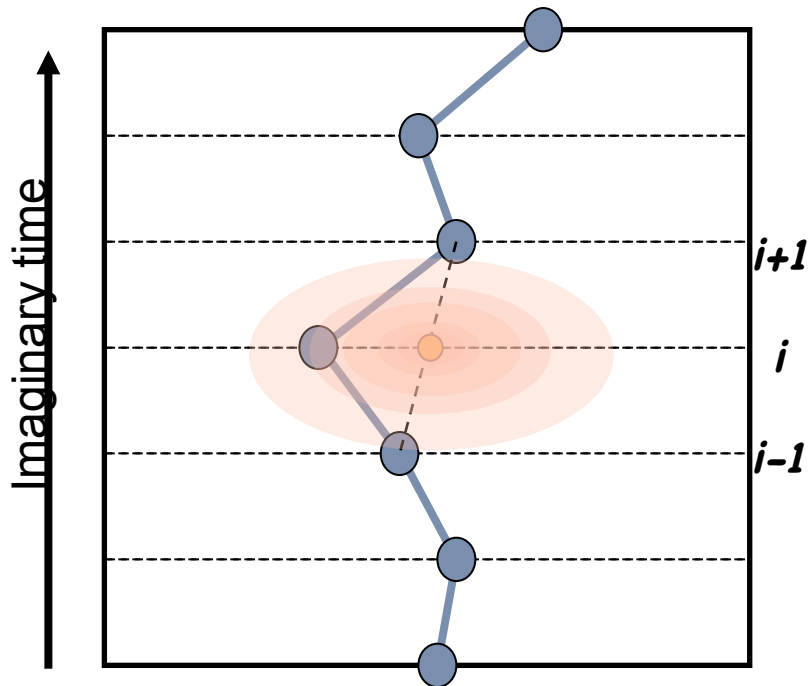
Distribution of "beads" for noninteracting particles

$$P(\vec{r}_i) = \frac{\rho(\vec{r}_{i-1},\vec{r}_i,\tau)\ \rho(\vec{r}_i,\vec{r}_{i+1},\tau)}{Z}$$

Normalization from density matrix squaring property

$$\rho(\vec{r}_{i-1},\vec{r}_{i+1},2\tau) = \int d\vec{r}_i\ \rho(\vec{r}_{i-1},\vec{r}_i,\tau)\ \rho(\vec{r}_i,\vec{r}_{i+1},\tau)$$

The distribution $P(r_i)$ is Gaussian centered at the midpoint of r_{i-1} and r_{i+1}
Use the Box-Mueller formula to generate points r_i according to $P(r_i)$.

$$A(R_{old} \to R_{new}) = \min\left\{1, \frac{T(R_{old} \to R_{new})\ \pi(R_{old})}{T(R_{new} \to R_{old})\ \pi(R_{new})}\right\} = 1$$

Building a Browning Bridge
Method 1: Levy Construction

Multi-slice moves are more efficient!
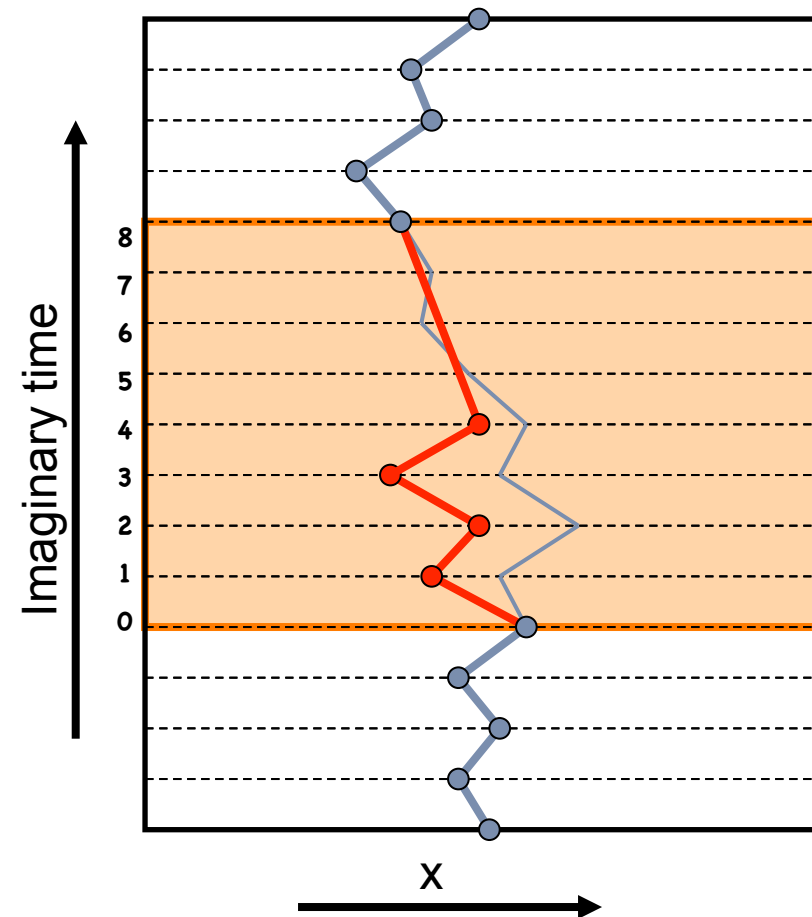
Step 0: Pick an imaginary time window
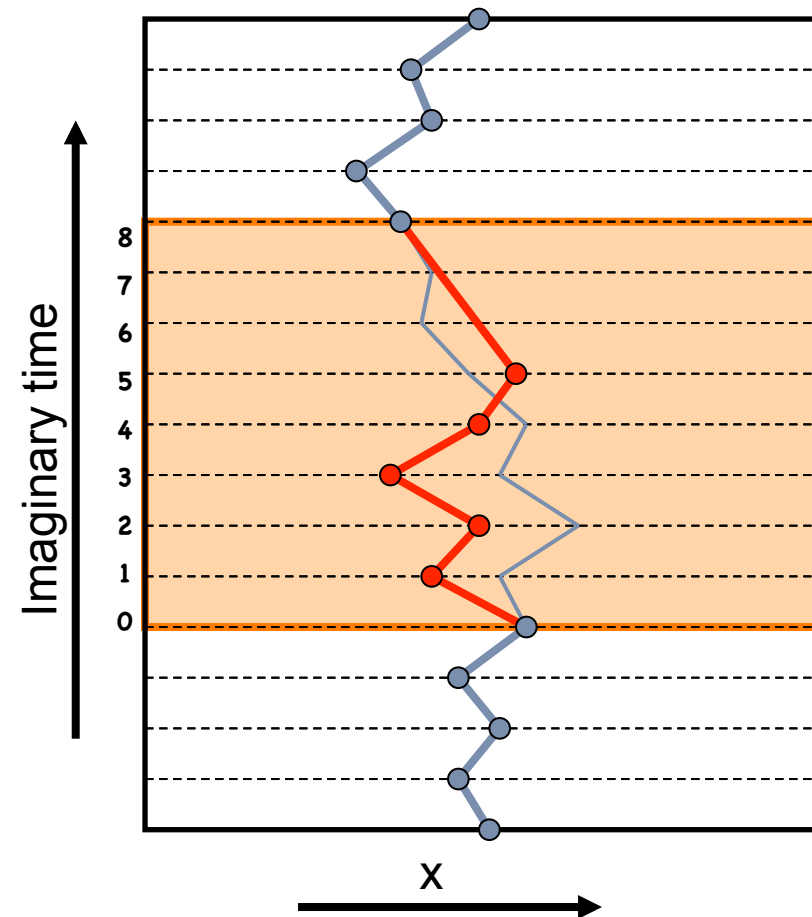**Step 1: Sample the first point r_1:**

$$P(\vec{r}_1) = \frac{\rho(\vec{r}_0,\vec{r}_1,\tau)\ \rho(\vec{r}_1,\vec{r}_8,7\tau)}{\rho(\vec{r}_0,\vec{r}_8,8\tau)}$$
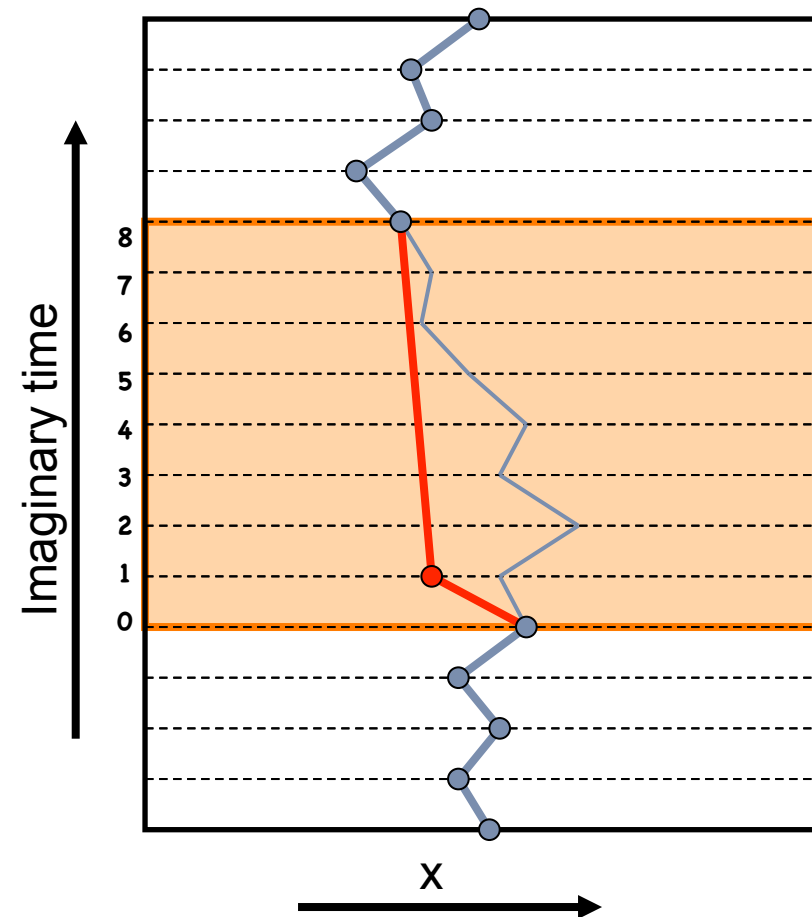
Imaginary time

X

Building a Browning Bridge
Method 1: Levy Construction

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window
Step 1: Sample the first point r_1
Step 2: Sample the second point r_2:

$$P(\vec{r}_2) = \frac{\rho(\vec{r}_1, \vec{r}_2, \tau)\ \rho(\vec{r}_2, \vec{r}_8, 6\tau)}{\rho(\vec{r}_1, \vec{r}_8, 7\tau)}$$

Imaginary time

8
7
6
5
4
3
2
1
0

X

Building a Browning Bridge
Method 1: Levy Construction

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window
Step 1: Sample the first point r_1
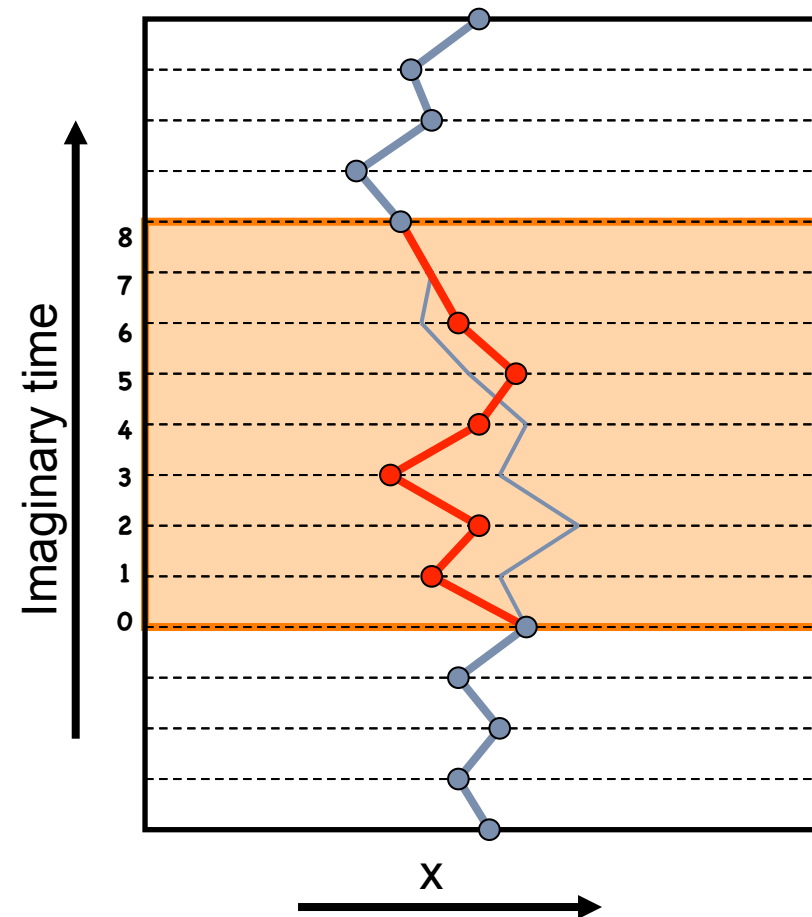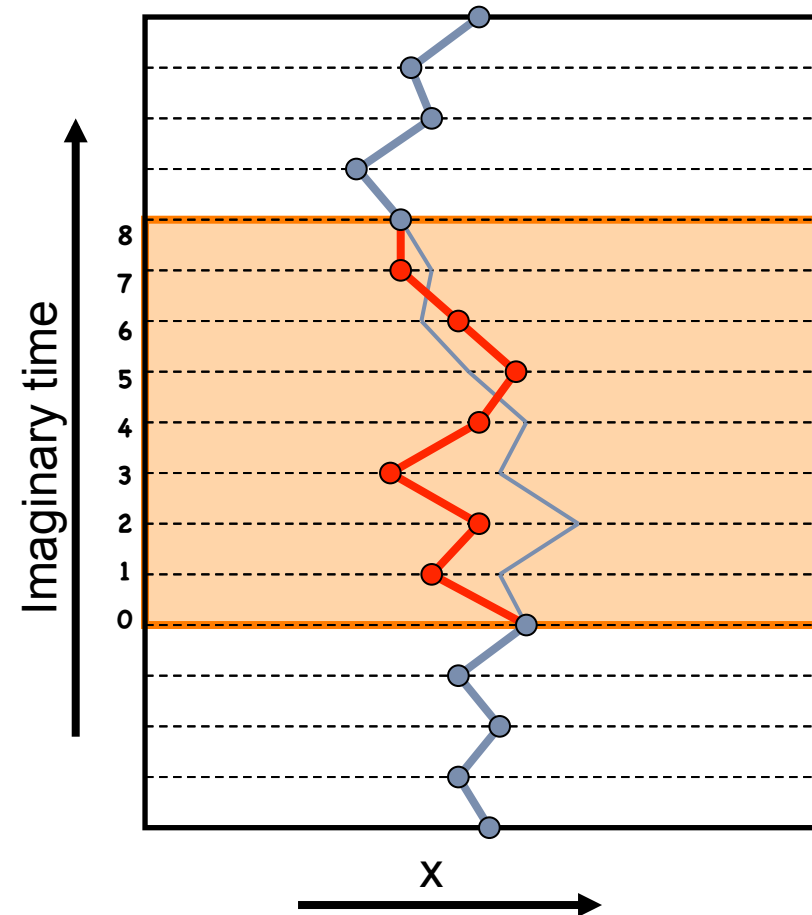Step 2: Sample the second point r_2
Step 3: Sample the third point r_3:

$$P(\vec{r}_3) = \frac{\rho(\vec{r}_2,\vec{r}_3,\tau)\ \ \rho(\vec{r}_3,\vec{r}_8,5\tau)}{\rho(\vec{r}_2,\vec{r}_8,6\tau)}$$
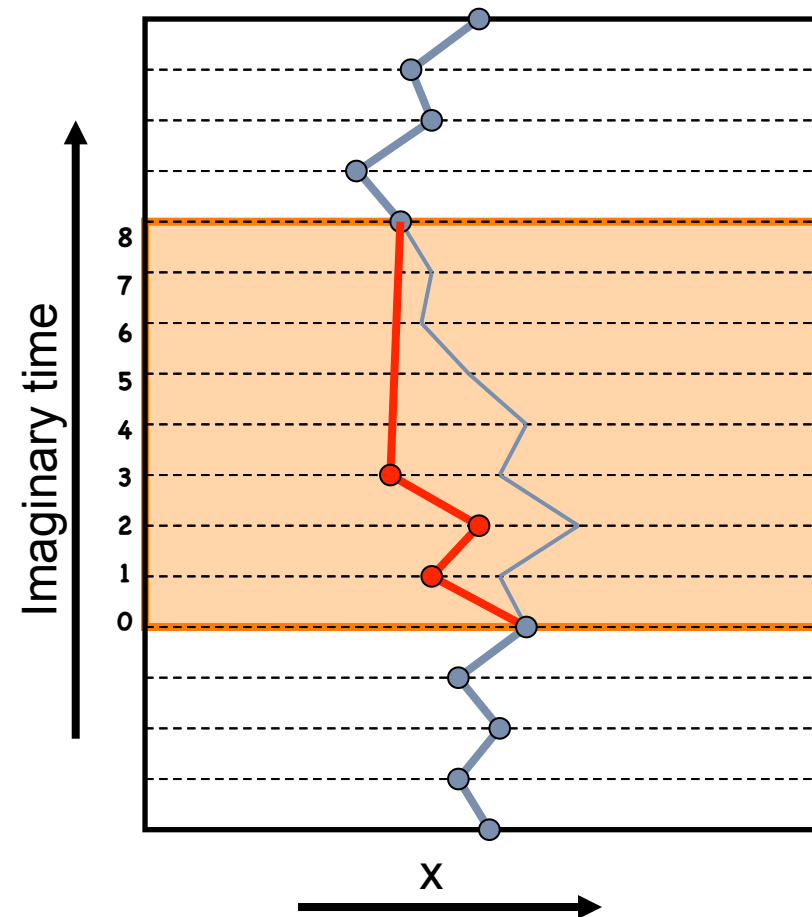
Building a Browning Bridge
Method 1: Levy Construction

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window
Step 1: Sample the first point r_1
Step 2: Sample the second point r_2
Step 3: Sample the third point r_3
Step 4: Sample the forth point r_4:

$$P(\vec{r}_4) = \frac{\rho(\vec{r}_3,\vec{r}_4,\tau)\ \rho(\vec{r}_4,\vec{r}_8,4\tau)}{\rho(\vec{r}_3,\vec{r}_8,5\tau)}$$

Building a Browning Bridge
Method 1: Levy Construction

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window
Step 1: Sample the first point r_1
Step 2: Sample the second point r_2
Step 3: Sample the third point r_3
Step 4: Sample the forth point r_4
Step 5: Sample the fifth point r_5 :

$$P(\vec{r}_5) = \frac{\rho(\vec{r}_4,\vec{r}_5,\tau)\ \rho(\vec{r}_5,\vec{r}_8,3\tau)}{\rho(\vec{r}_4,\vec{r}_8,4\tau)}$$
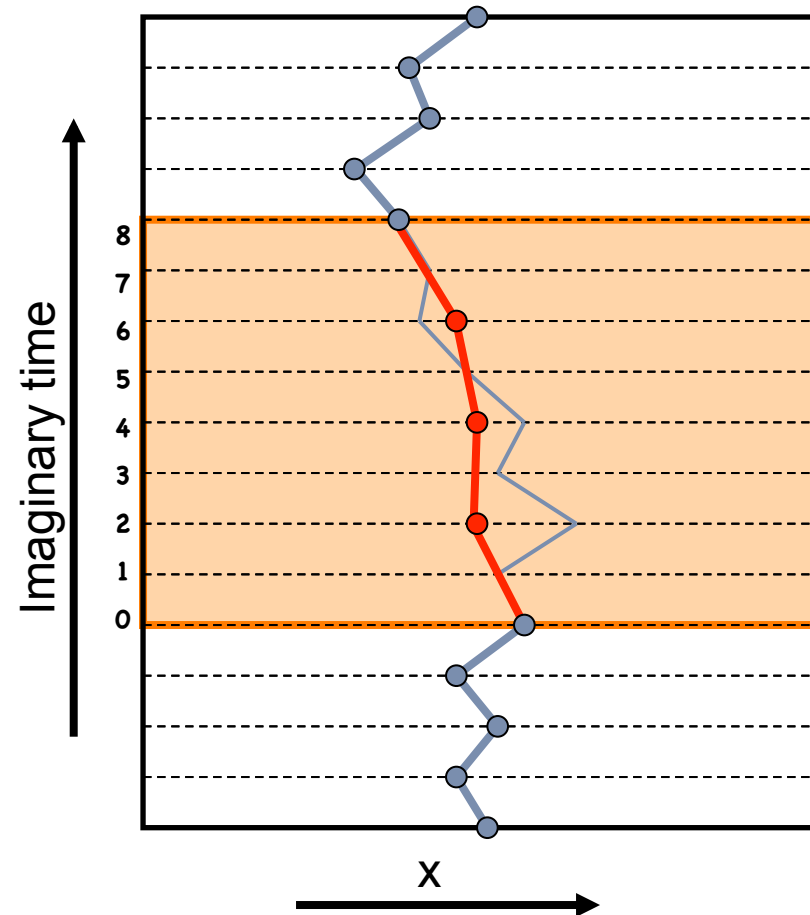
Building a Browning Bridge
Method 1: Levy Construction

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window
Step 1: Sample the first point r_1
Step 2: Sample the second point r_2
Step 3: Sample the third point r_3
Step 4: Sample the forth point r_4
Step 5: Sample the fifth point r_5
Step 6: Sample the sixth point r_6 :

$$P(\vec{r}_6) = \frac{\rho(\vec{r}_5,\vec{r}_6,\tau)\ \rho(\vec{r}_6,\vec{r}_8,2\tau)}{\rho(\vec{r}_5,\vec{r}_8,3\tau)}$$

Building a Browning Bridge
Method 1: Levy Construction

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window
Step 1: Sample the first point r_1
Step 2: Sample the second point r_2
Step 3: Sample the third point r_3
Step 4: Sample the forth point r_4
Step 5: Sample the fifth point r_5
Step 6: Sample the sixth point r_6
Step 7: Sample the seventh point r_7 :

$$P(\vec{r}_7) = \frac{\rho(\vec{r}_6,\vec{r}_7,\tau)\ \ \rho(\vec{r}_7,\vec{r}_8,\tau)}{\rho(\vec{r}_6,\vec{r}_8,2\tau)}$$

Imaginary time

X

Building a Browning Bridge
Method 1: Levy Construction

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window
Step 1: Sample the first point r_1
Step 2: Sample the second point r_2
Step 3: Sample the third point r_3
Step 4: Sample the forth point r_4
Step 5: Sample the fifth point r_5
Step 6: Sample the sixth point r_6
Step 7: Sample the seventh point r_7

Last step: Accept or reject decision is based on the potential action since it was not considered in the Levy construction.
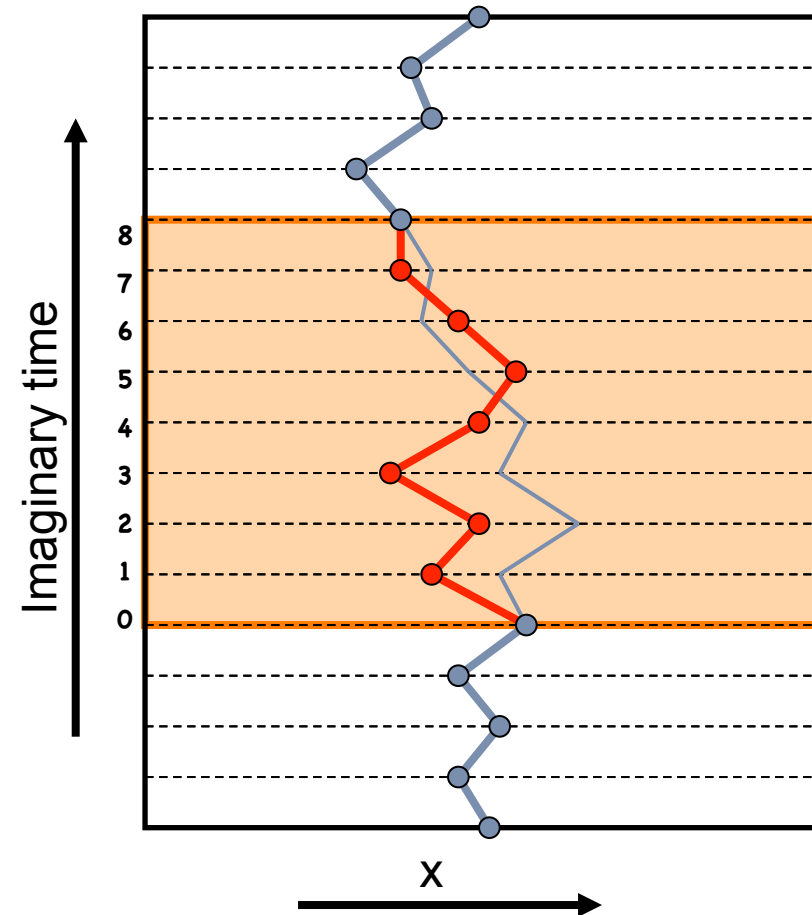
Building a Browning Bridge
# Method 2: Bisection

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window
Step 1: Sample the first point r_4:

$$P(\vec{r}_i) = \frac{\rho(\vec{r}_{i-4},\vec{r}_i,4\tau)\ \rho(\vec{r}_i,\vec{r}_{i+4},4\tau)}{\rho(\vec{r}_{i-4},\vec{r}_{i+4},8\tau)}$$
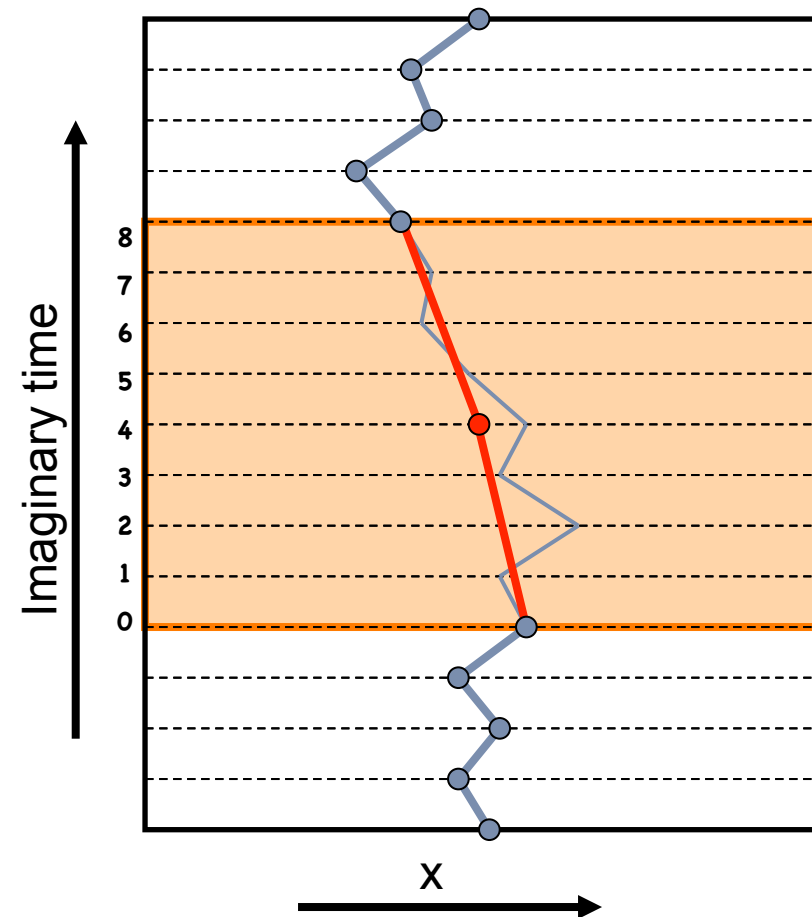
Building a Browning Bridge
Method 2: Bisection

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window
Step 1: Sample the first point r_4
Step 2: Sample points r_2 and r_6:

$$P(\vec{r}_i) = \frac{\rho(\vec{r}_{i-2},\vec{r}_i,2\tau)\;\rho(\vec{r}_i,\vec{r}_{i+2},2\tau)}{\rho(\vec{r}_{i-2},\vec{r}_{i+2},4\tau)}$$

Imaginary time

X

Building a Browning Bridge
Method 2: Bisection

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window
Step 1: Sample the first point r_4
Step 2: Sample points r_2 and r_6
Step 3: Sample the points r_1 r_3 r_5 r_7:

$$P(\vec{r}_i) = \frac{\rho(\vec{r}_{i-1},\vec{r}_i,\tau)\ \rho(\vec{r}_i,\vec{r}_{i+1},\tau)}{\rho(\vec{r}_{i-1},\vec{r}_{i+1},2\tau)}$$
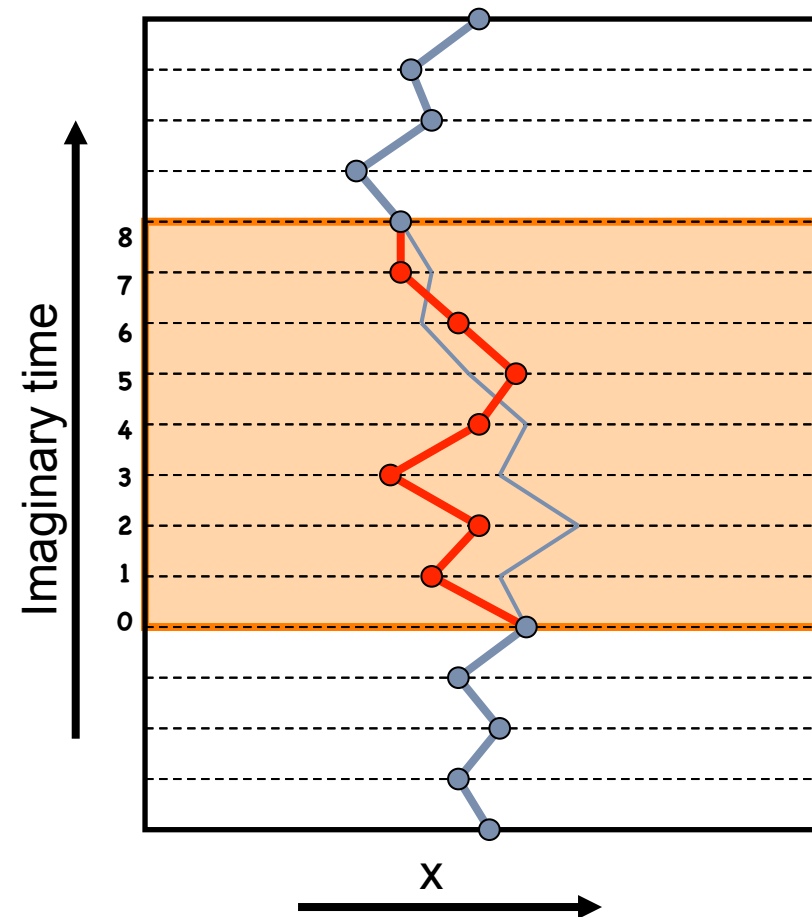
Building a Browning Bridge
Method 2: Bisection

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window
Step 1: Sample the first point r_4
Step 2: Sample points r_2 and r_6
Step 3: Sample the points r_1 r_3 r_5 r_7

Last step: Accept or reject based on the potential action since it was not considered in the bisection.
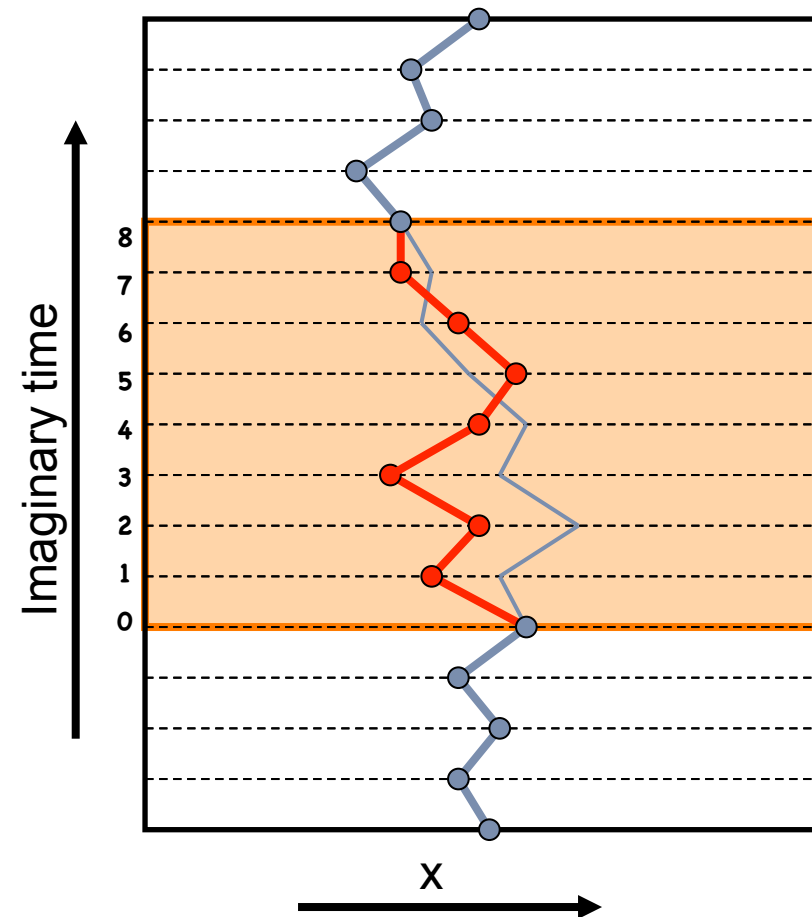
Building a Browning Bridge
Method 2: Bisection

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window
Step 1: Sample the first point r_4
Step 2: Sample points r_2 and r_6
Step 3: Sample the points r_1 r_3 r_5 r_7

Huge efficiency gain by prerejection of unlikely paths using the potential action already at steps 1 and 2.
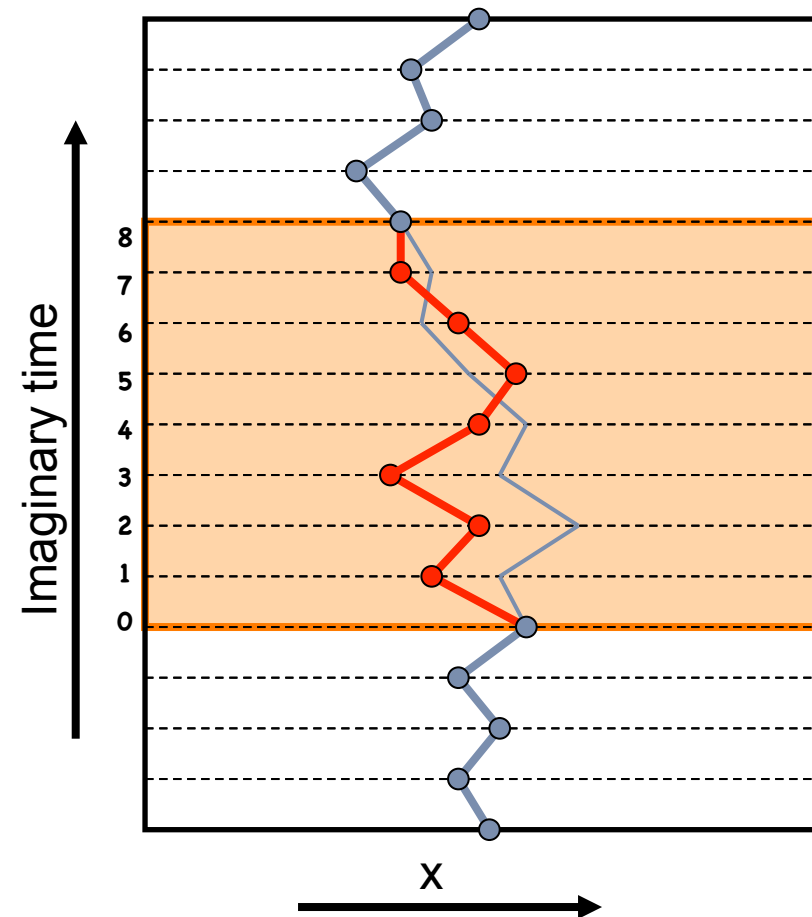
Reducing the number of time slices by making a better action: The pair action method

$$\langle R | \hat{\rho} | R' \rangle = \oint_{R \to R'} dR_t e^{-S[R_t]}$$

$$S[R_t] = \sum_{i=1}^{M} \frac{(R_{i+1} - R_i)^2}{4\lambda\tau} + \frac{\tau}{2}\left[V(R_i) + V(R_{i+1})\right]$$

Pair action method:

$$\rho(R, R', \tau) = \exp\{-S_I(R, R', \tau)\} \prod_i \rho_0(r_i, r_i', \tau)$$

$$\exp\{-S_I(R, R', \tau)\} \approx \exp\left\{-\sum_{i<j} s_I(r_{ij}, r_{ij}', \tau)\right\} = \prod_{i<j} \frac{\rho(r_{ij}, r_{ij}', \tau)}{\rho_0(r_{ij}, r_{ij}', \tau)}$$

The many-body action is approximated a sum over pair interactions. The pair action $s_I(r_{ij}, r_{ij}', \tau)$ can be computed exactly by solving the two-particle problem.

Three methods to derive the pair action $s_I(r_{ij}, r'_{ij}, \tau)$

(1) From definition: Sum over eigenstates:

$$\rho(R, R', \beta) = \sum_S e^{-\beta E_S} \Psi_S^*(R) \Psi_S(R')$$

One needs to know all eigenstates analytically (free and bound). They are not known in most cases. Only derived for Coulomb problem [Pollock. Comm. Phys. Comm. 52 (1988) 49].

(2) Matrix squaring:

$$\rho_l(r, r', \tau) = \int dr'' \, \rho_l(r, r'', \tau/2) \, \rho_l(r'', r', \tau/2)$$

One starts with a high temperature approximation and applies the squaring formula successively (10 times) to obtain the pair density matrix at temperature $1/\tau$. Advantage: works for all potentials, provides diagonal and all off-diagaonal elements at once. Disadvantage: Integration is performed on a grid. Grid error must be carefully controlled.

(3) Feynman-Kac formula:

See next slide. Advantage: Very simple and robust. Numerical accuracy can be easily controlled. Disadvantages: Does not work for potentials with negative singularities (e.g. attractive Coulomb potential), off-diagonal elements require more work.

Use a browning bridge to derive the exact 2-particle action: Feynman-Kac

The exact action can be derived by averaging the potential action of free particle paths generated with a browning bridge. Feynman-Kac formula:

$$\rho(r,r',\beta) \equiv \exp[-S(r,r',\beta)] \equiv \exp[-(S_0 + S_I)] = \rho_0(r,r',\beta) \left\langle \exp\left[-\int dt\, V[r(t)]\right]\right\rangle_{BB}$$
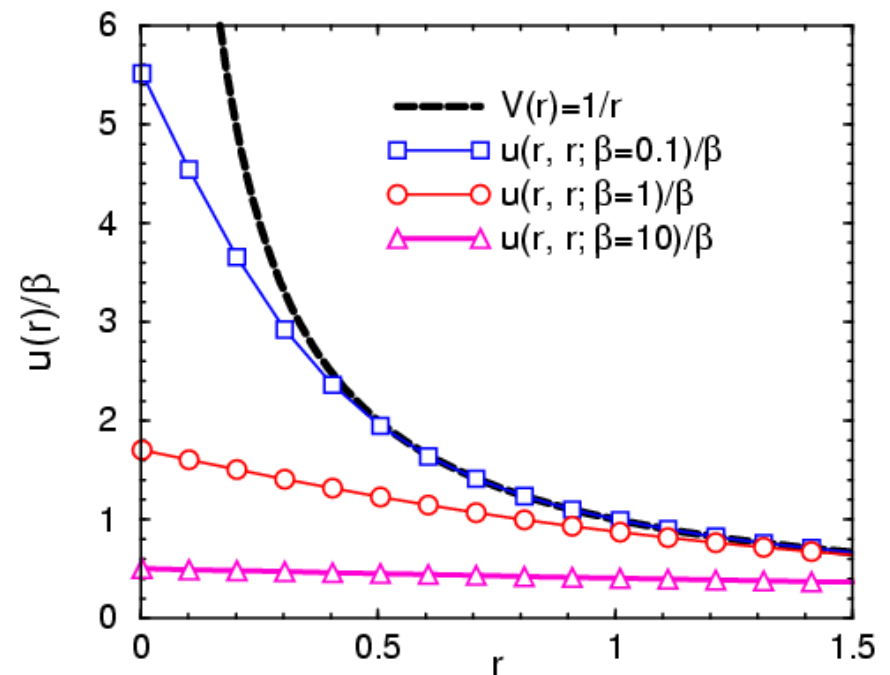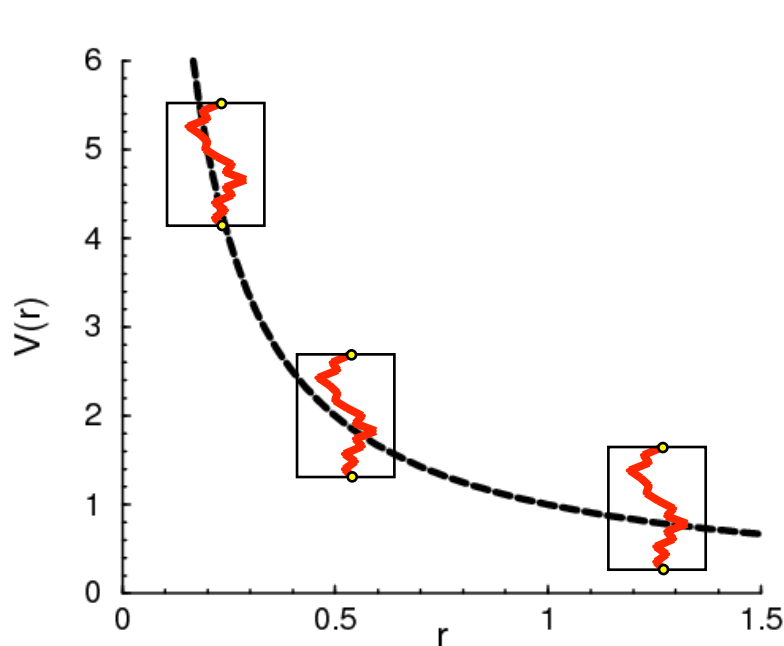
IV. Do we need path integrals to compute phonons?

High-Pressure Phases of Solid CO$_2$

Bonev et al. PRL 91 (2003) 065501

Density functional calculations:

- Full structural optimization started from experimental geometries
- Phonon spectra from linear response
- Gibbs free energies

Quasi-harmonic approximation:

$$E = E_0 + \tfrac{1}{2}\sum_{ij}(r_i - r_i^o)(r_j - r_j^o)\frac{\partial^2 E}{\partial r_i \partial r_j}$$

Phonon frequencies of eigen modes: $\omega_{k,v}$

$$E = E_0 + \sum_{k,v}\tfrac{1}{2}h\omega + \sum_{k,v}\frac{h\omega}{e^{+\beta h\omega}-1}$$

$$G = E_0 + \sum_{k,v}\tfrac{1}{2}h\omega + \sum_{k,v}\ln\left(1-e^{-\beta hw}\right) + PV$$
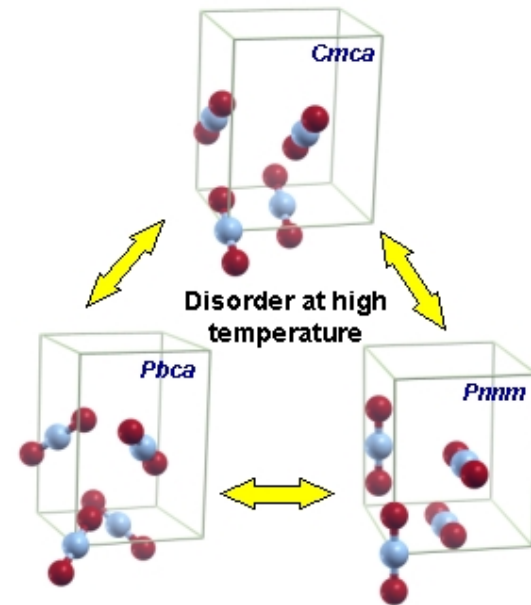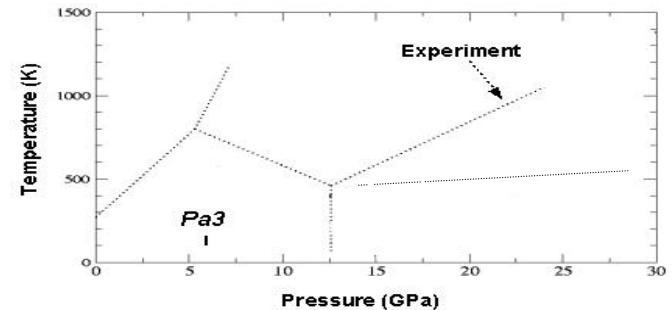
DFT helps to identify Raman modes

19 GPa

E_g

B_{1g}

E_g

B_{1g}

100   200   300   400

E_g

B_{1g}
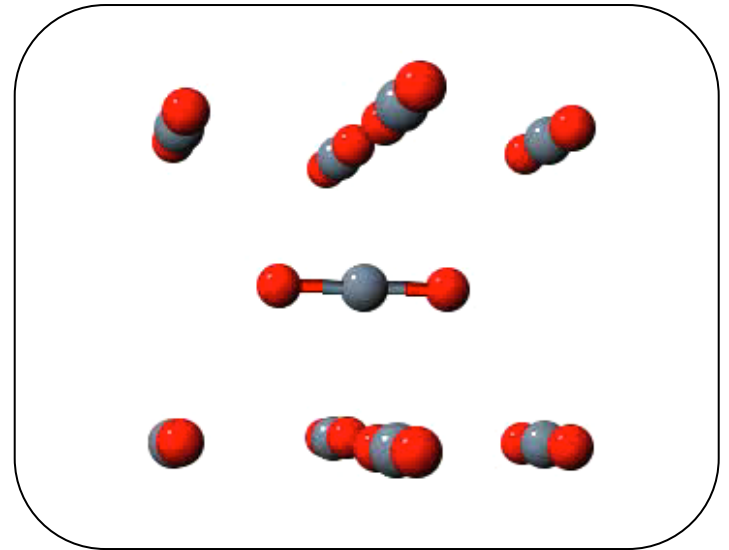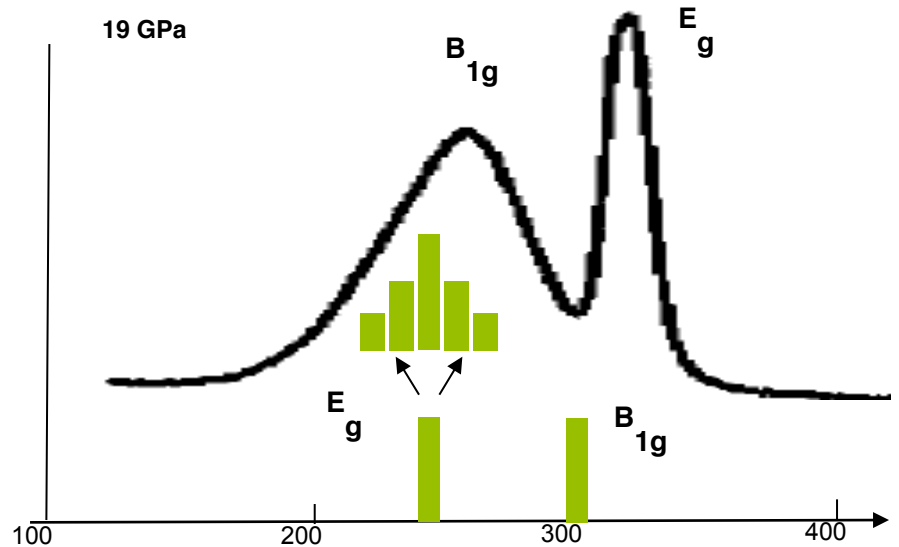
0.1 GPa stress anisotropy ⟹ 20 cm-1 splitting of E_g

lift the degeneracy   double degeneracy
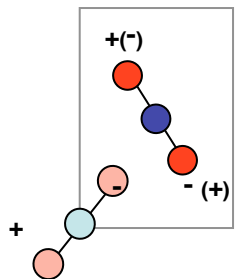
+(⁻)   +(⁻)

orthorhombic
deformation

⁻   ⁻ (+)   ⁻   ⁻ (+)

+   +
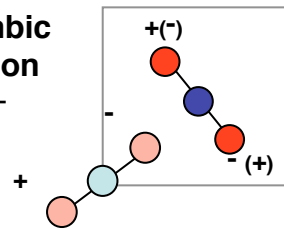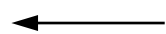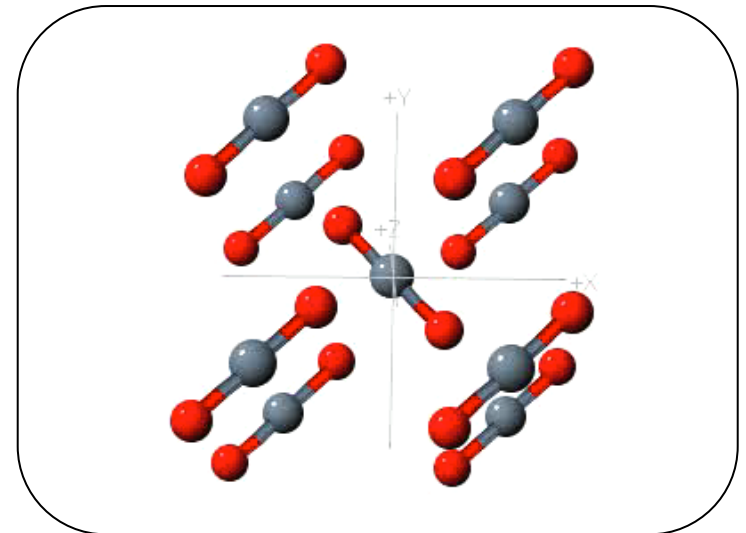
V. Path integrals combined with DFT forces: study the zero-point motion of nuclei

PIMD for the nuclei based on forces derived with DFT:
Charged water complexes $H_5O_2^+$ and $H_3O_2^-$

On the Quantum Nature of the Shared Proton in Hydrogen Bonds

Mark E. Tuckerman, Dominik Marx, Michael L. Klein, Michele Parrinello
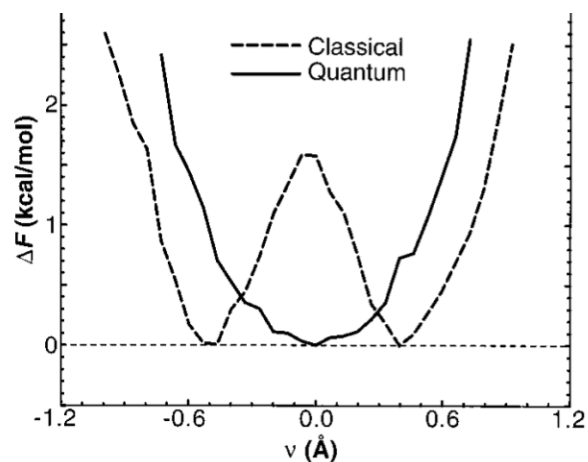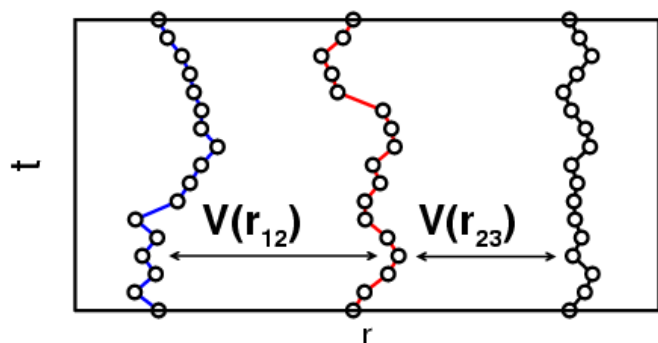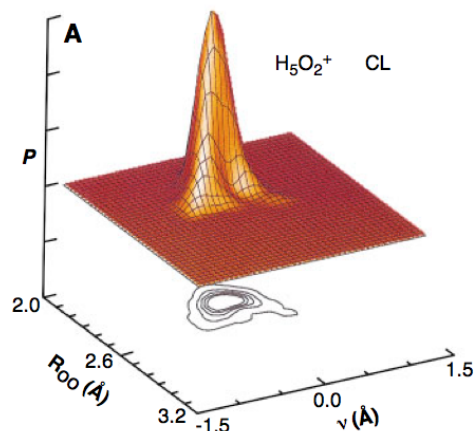
Classical nuclei   Quantum nuclei
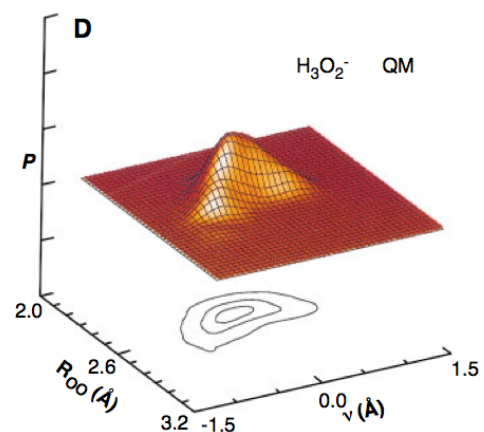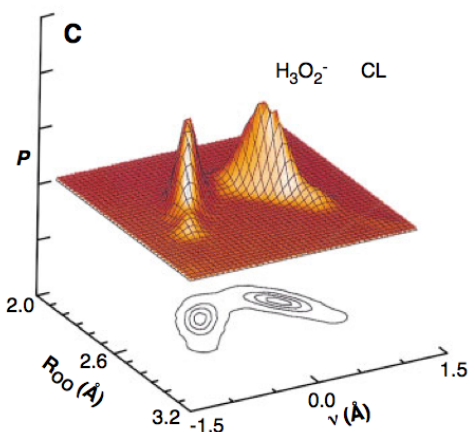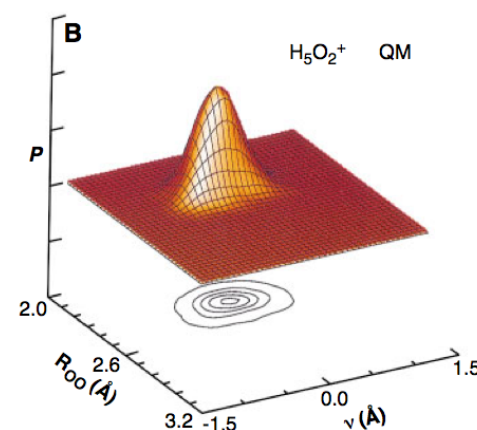
Fig. 2. Distribution functions $P(R_{OO}, \nu)$ as computed from molecular dynamics simulations at 300 K for (**A**) classical $H_5O_2^+$, (**B**) quantum $H_5O_2^+$, (**C**) classical $H_3O_2^-$, and (**D**) quantum $H_3O_2^-$ with peak and the contour heights (in arbitrary units) are identical in all panels. R_{OO} represents the oxygen-oxygen distance, and $\nu = r_{O_aH^*} - r_{O_bH^*}$ is the asymmetric stretch coordinate obtained from the two oxygen-shared hydrogen distances $r_{O_aH^*}$ and $r_{O_bH^*}$. The three-body system $O_a \cdots H^* \cdots O_b$ is confocal elliptic with

PIMD for the nuclei based on forces derived with DFT:
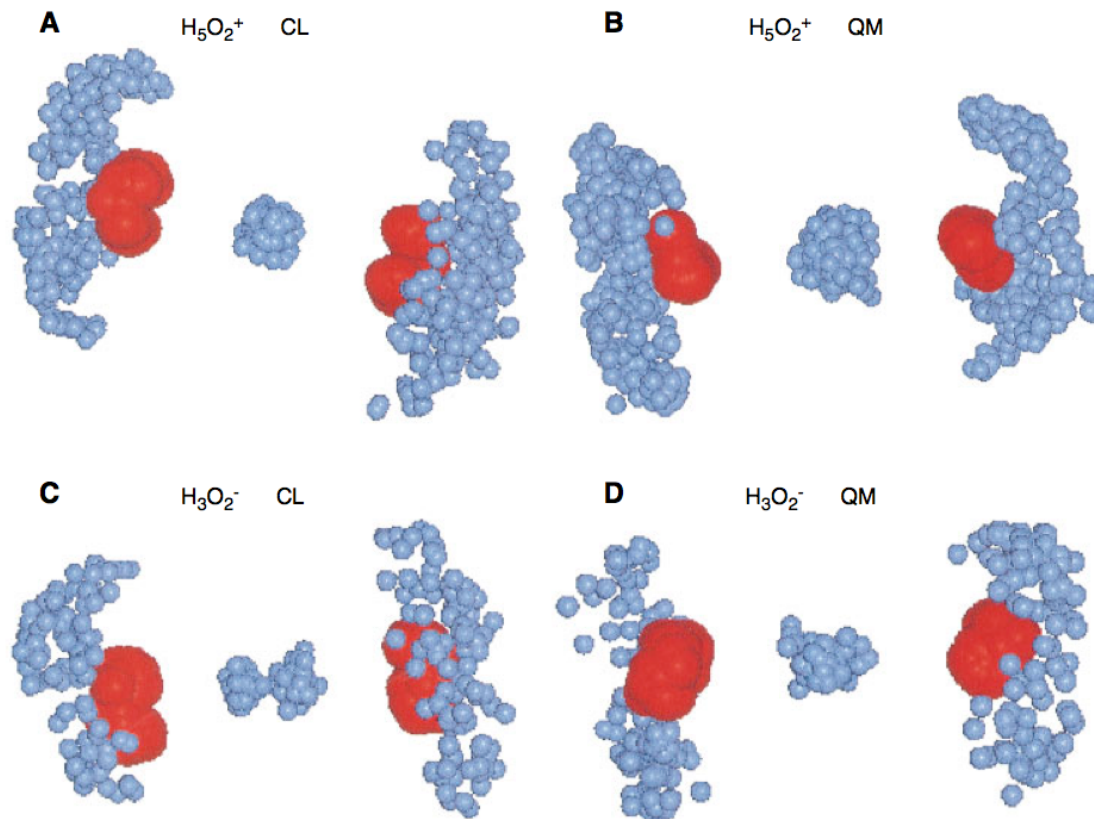## Picture explains details of the geometry

Fig. 1. Representative configurations from molecular dynamics runs at 300 K superimposed on each other for (**A**) classical (CL) $H_5O_2^+$, (**B**) quantum (QM) $H_5O_2^+$, (**C**) classical $H_3O_2^-$, and (**D**) quantum $H_3O_2^-$. All particles of every (replica) configuration were rotated on a common space-fixed axis defined by the OO vector for one particular configuration. The red and blue spheres denote oxygen and hydrogen atoms, respectively.

PIMD for the nuclei based on forces derived with DFT:
(or how to make water softer)

The nature and transport mechanism of hydrated hydroxide ions in aqueous solution

Mark E. Tuckerman*, Dominik Marx† & Michele Parrinello‡§
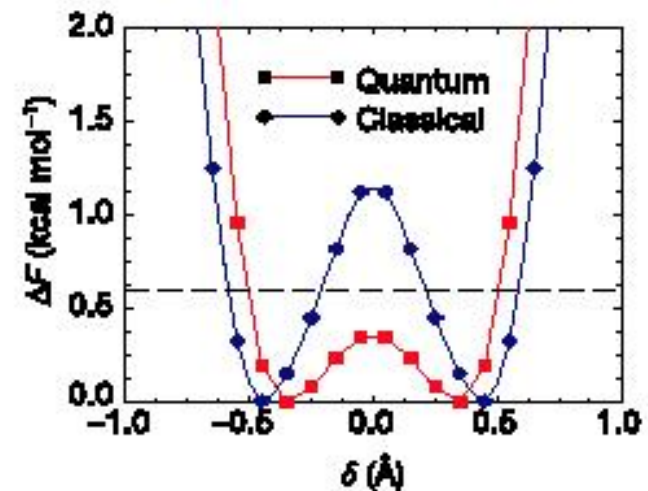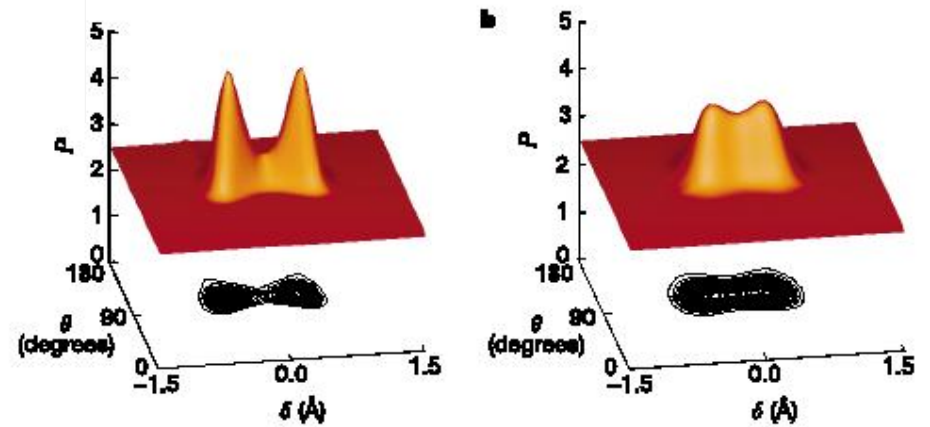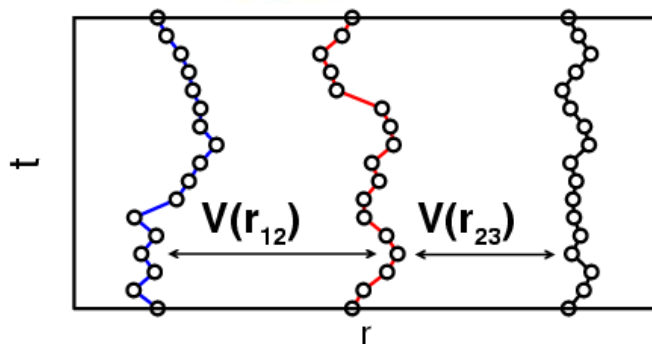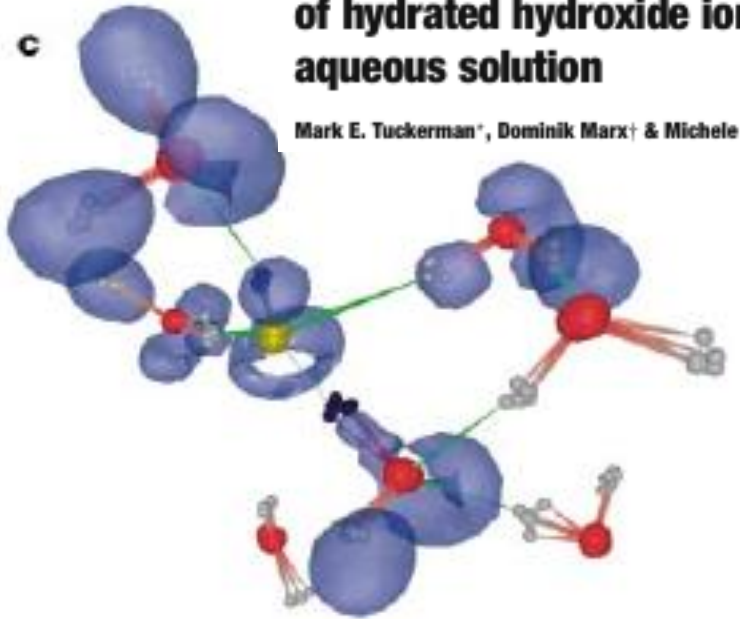
VI. PIMC of the Wigner crystal

Example for PIMC with distinguishable particles: Melting of Atomic Hydrogen

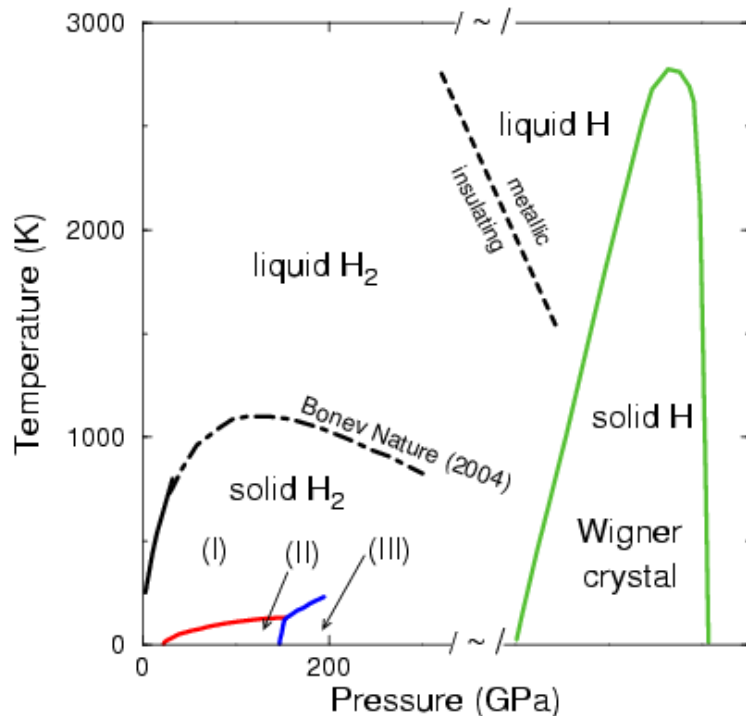**At extremely high pressure, atomic hydrogen is predicted to form a Wigner crystal of protons (b.c.c. phase)**

Electron gas is highly degenerate. Model calculation for a one-component plasma of protons.

Coulomb simulations have been preformed by Jones and Ceperley, Phys. Rev. Lett. (1996).

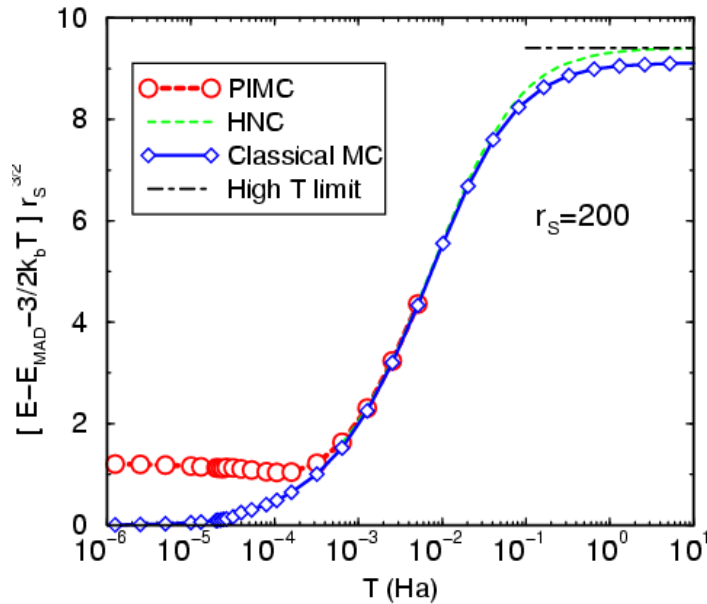Here, we include electron screening effects by including Thomas Fermi screening leading to a Yukawa pair potential:

$$V(r) = \frac{Z^2}{r} e^{-r / D_s}$$

1) Distinguish between classical and quantum melting.
2) Study anharmonic effects in the crystal.

Phase diagram showing Temperature (K) from 0 to 3000 versus Pressure (GPa). Regions labeled: liquid H₂, liquid H, metallic, insulating, solid H₂ (I) (II) (III), solid H, Wigner crystal. Bonev Nature (2004).

Simulation of Hydrogen Melting
Wigner crystal of protons studied with PIMC

Compare classical Monte Carlo with PIMC results:
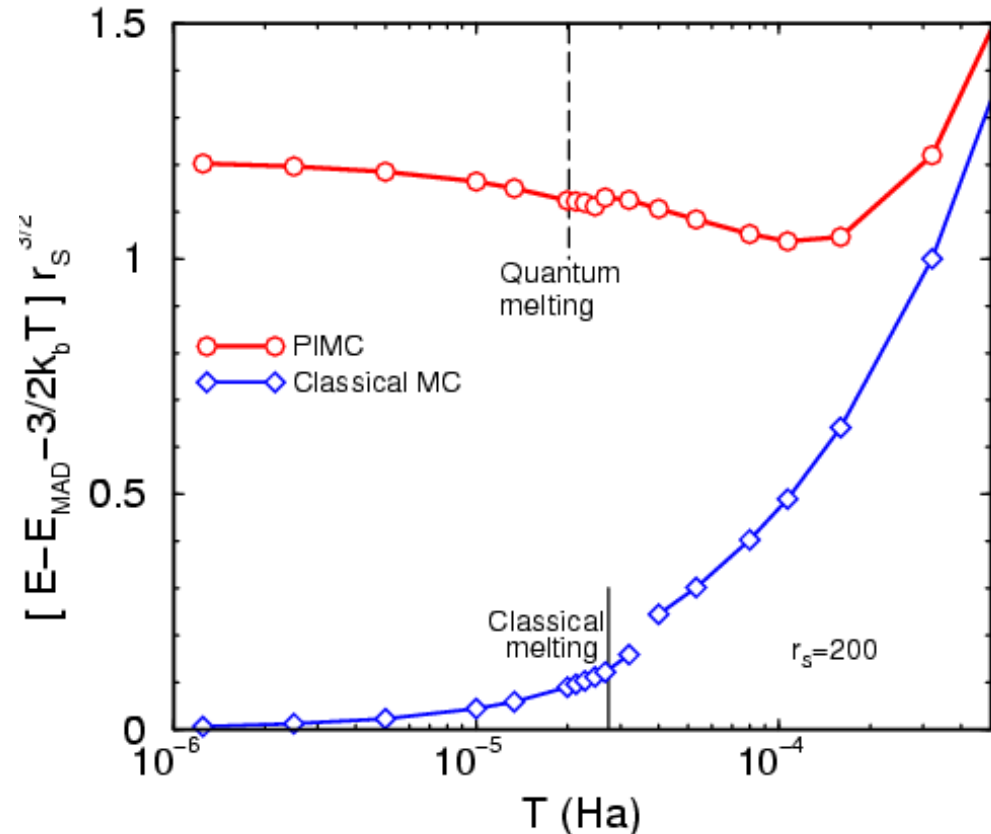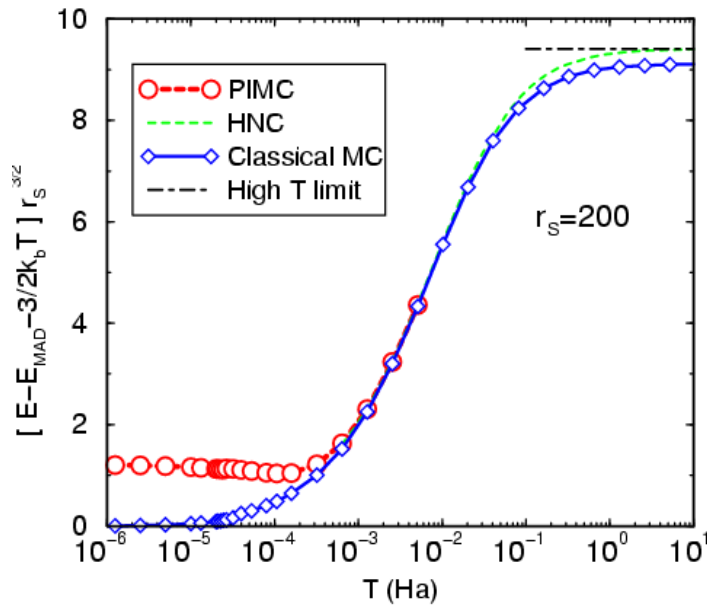
1) **At high T**, all particles behave **classically**, if the thermal de Broglie length is small:

$$r_S \gg \lambda_d \quad, \quad \lambda_d = \sqrt{\frac{h^2}{2\pi\, m\, k_b T}}$$

2) At low T, quantum simulations show a much higher energy due to the **zero point motion**.
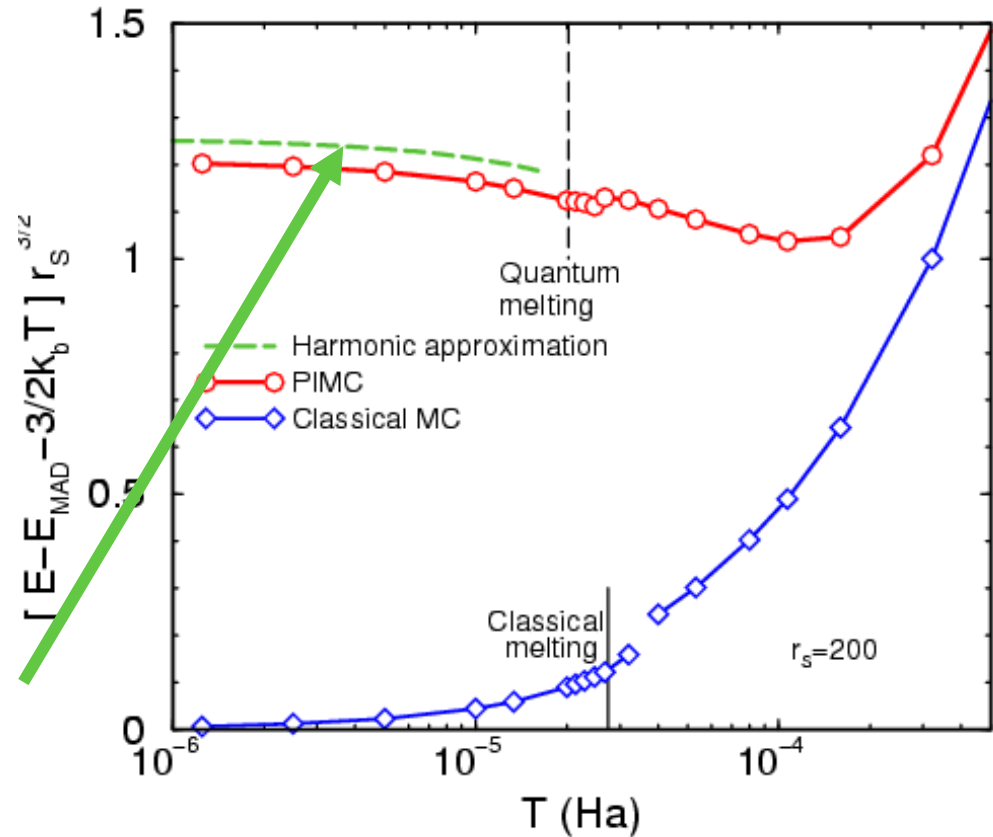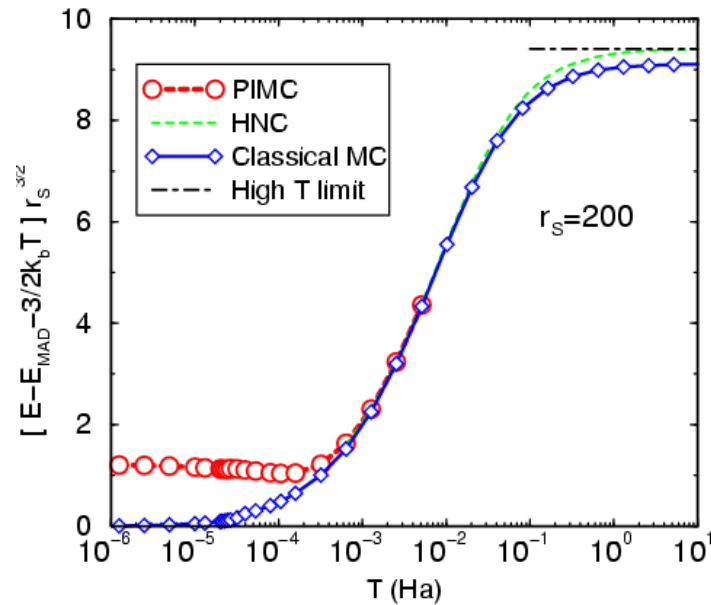
Simulation of Hydrogen Melting
Wigner crystal of protons studied with PIMC

1) **PIMC leads to an exact solution of the Schroedinger equation at any T (for distinguishable particles)**

2) **Thermal lattice vibrations are treated exactly (PIMC can only study equilibrium properties, no dynamics)**

Simulation of Hydrogen Melting
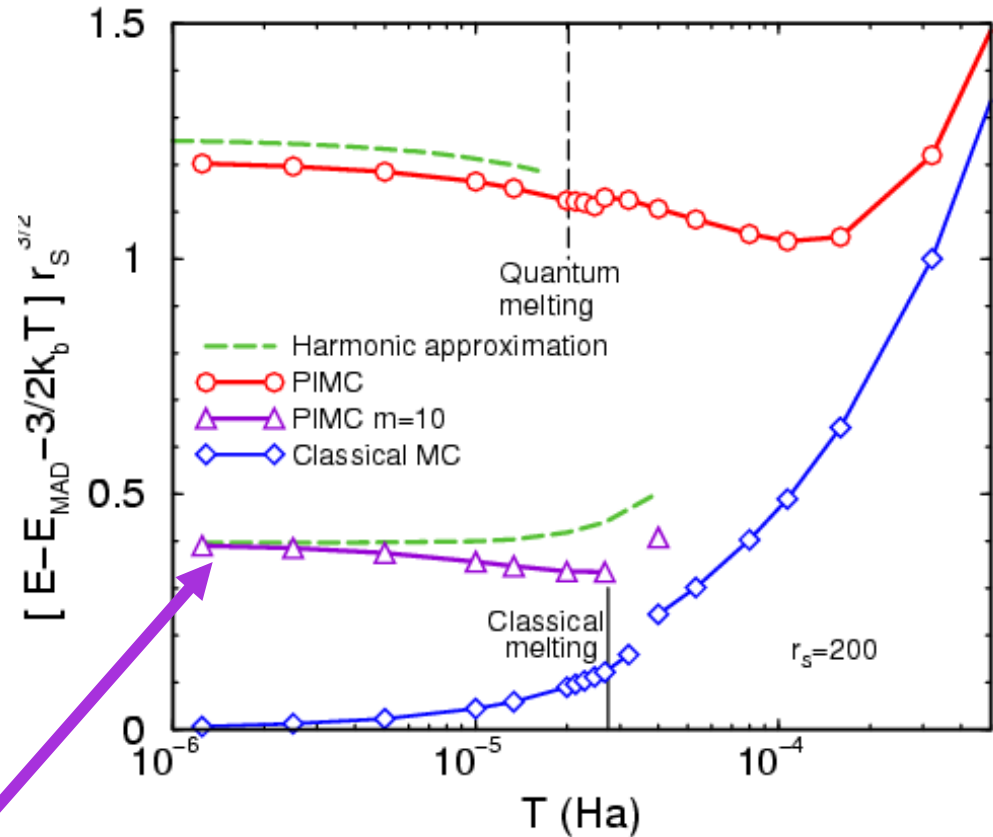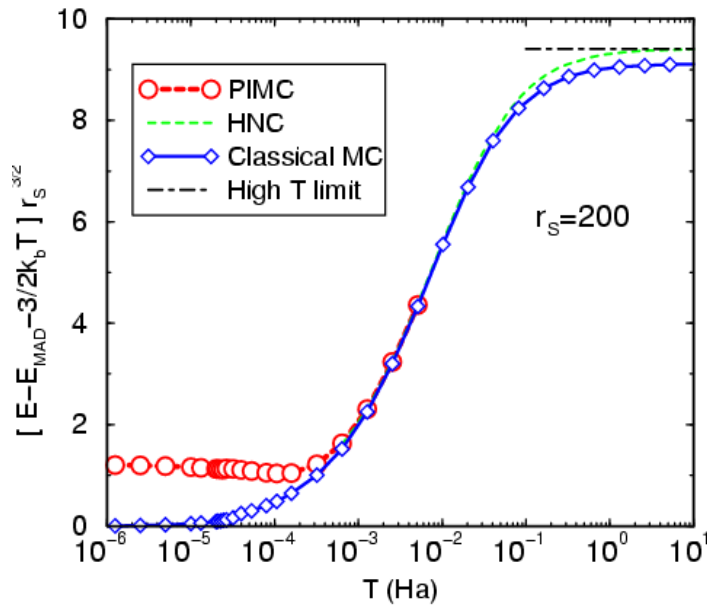## Comparison with harmonic lattice approximation

Harmonic lattice approximation:

$$D_{ij} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 V}{\partial R_i \partial R_j} \quad , \quad \left| D - 1\omega^2 \right| = 0$$

In the **HLA**, the protons are too localized because they are
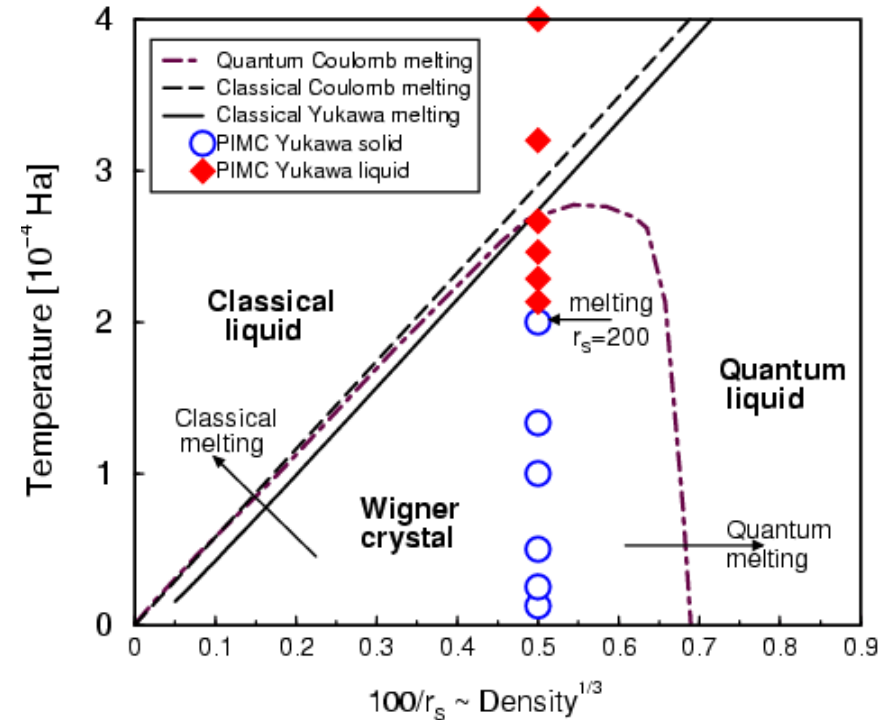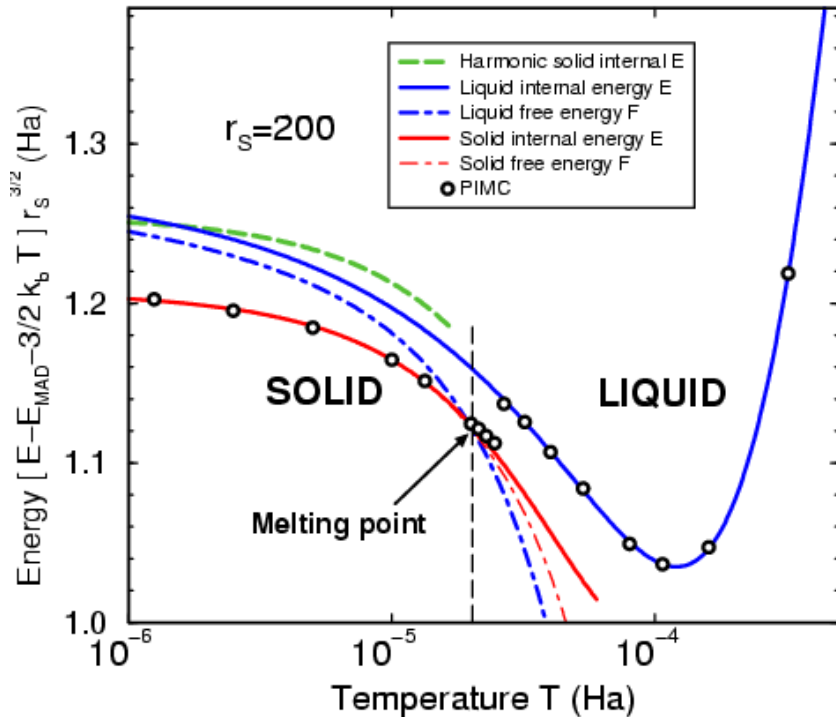light particle, probe the anharmonic regions of the potential.

Simulation of Hydrogen Melting
Wigner crystal of protons studied with PIMC

For heavier particles, the **HLA** works much better.

Free energy calculations predict that melting temperature is reduced by quantum effects

Free energies by thermodynamic integration of the internal energy

$$\beta_1 F(\beta_1) - \beta_0 F(\beta_0) = \int E(\beta)\ d\beta$$

Quantum motion of hydrogen nuclei reduces the melting temperature.

Militzer, Graham, Journal of Physics and Chemistry of Solids, **67** (2006) 2136, (cond-mat)

The End