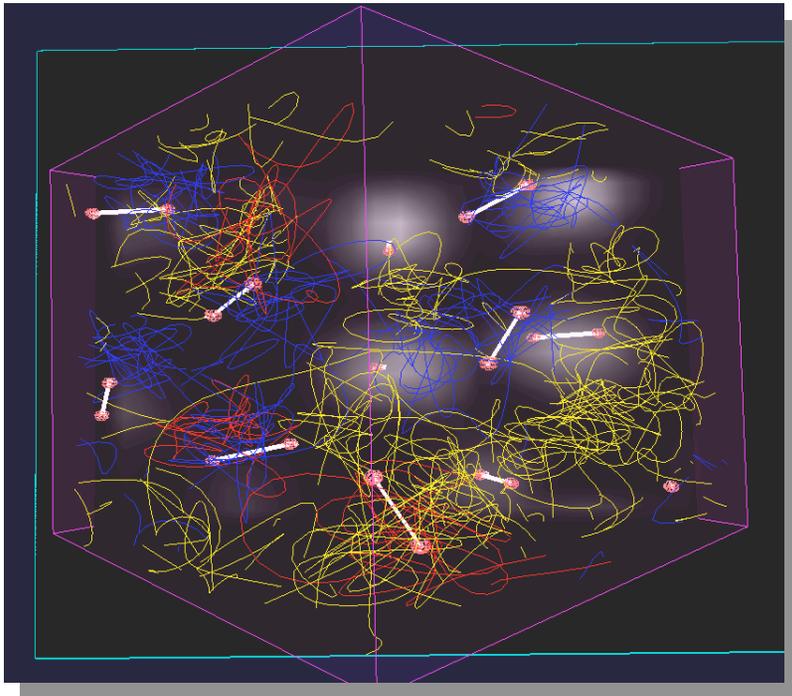


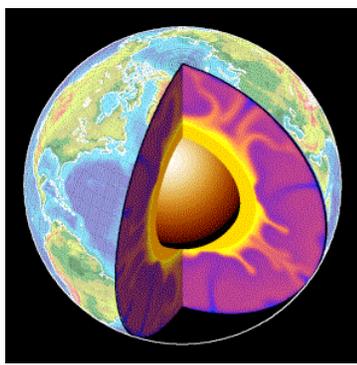
Path Integral Monte Carlo I

Summer school “QMC from Minerals and Materials to Molecules”

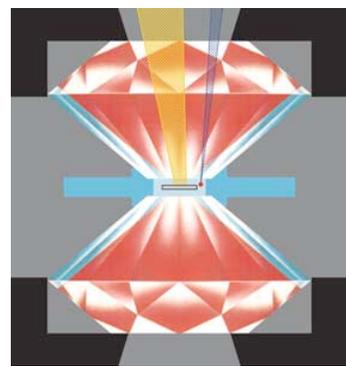


Burkhard Militzer

Geophysical Laboratory
Carnegie Institution of Washington
militzer@gl.ciw.edu
<http://militzer.gl.ciw.edu>



Study earth materials
High pressure experiments
Now also astrobiology



Diamond anvil cell exp.:
Ho-kwang Mao,
Russell J. Hemley

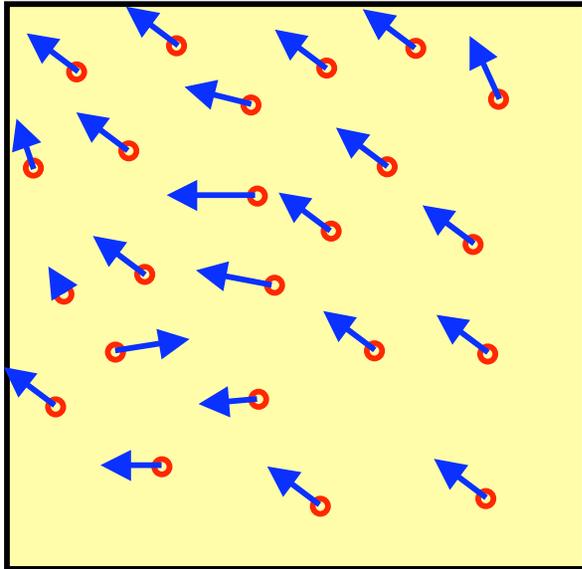
Original mission: Measure Earth's magnetic field (Carnegie ship)
Today: astronomy (Vera Rubin, Paul Butler,...) and isotope geochemistry

PIMC: Outline of presentations

- 1: PIMC for distinguishable particles (BM)
- 2: Lab on distinguishable particles (BM)
- 3: PIMC for bosons (BM)
- 4: Bosonic applications of PIMC (BM)
- 5: PIMC for fermions (David Ceperley)
- 6: Lab on bosonic application (Brian Clark, Ken Esler)

Molecular Dynamics (MD)

Simulate the motion of the atoms **in real time**



Pair potentials:

Forces on the atom,
Newton's law:

Change in velocity:

Change in position:

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

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

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

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

Microcanonical ensemble: Total energy is constant: $E=K+V$ but K and V fluctuate:

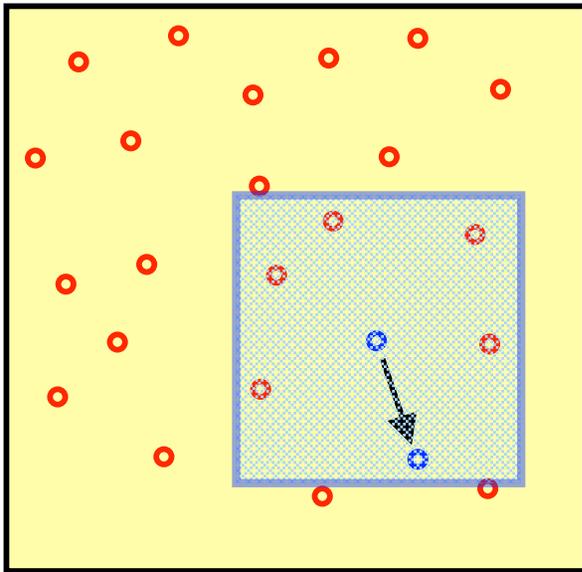
$$\langle K \rangle = \sum \frac{1}{2} m \langle \vec{v}^2 \rangle = \frac{3}{2} N k_b T$$

$$\langle V \rangle = \left\langle \sum_{i>j} V(r_i, r_j) \right\rangle$$

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

Monte Carlo (MC)

Generate states in the microcanonical ensemble



Pair potentials:

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

Probability of configuration

$$\pi(R) = \frac{1}{Z} \exp\left[-\frac{V(R)}{k_b T}\right]$$

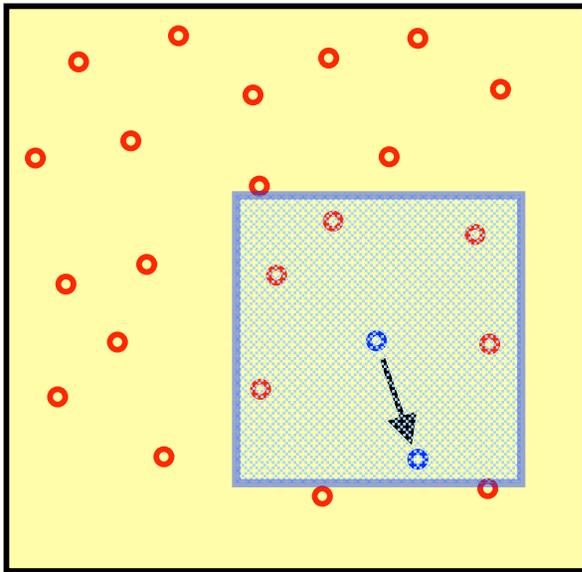
Metropolis algorithm (1953):

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

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

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, \dots

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

The Boltzmann factor is absorbed into the generated ensemble.

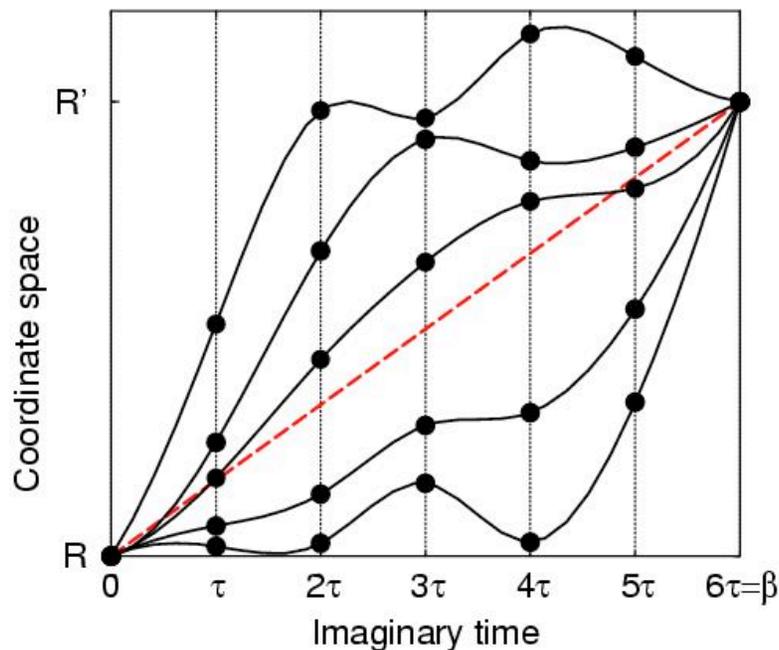
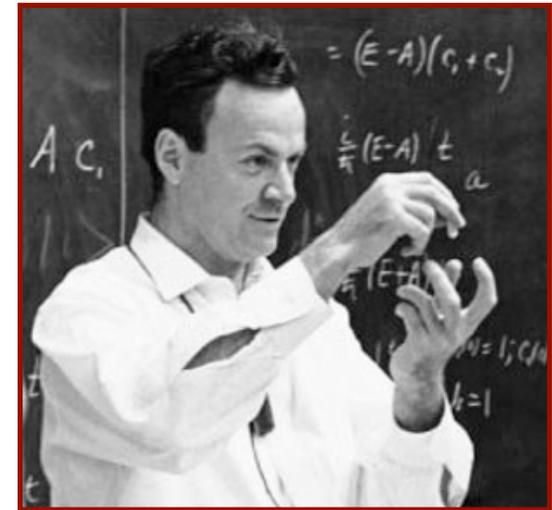
Quantum systems at finite temperature: Richard Feynman's path integrals

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 $T>0$)

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

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

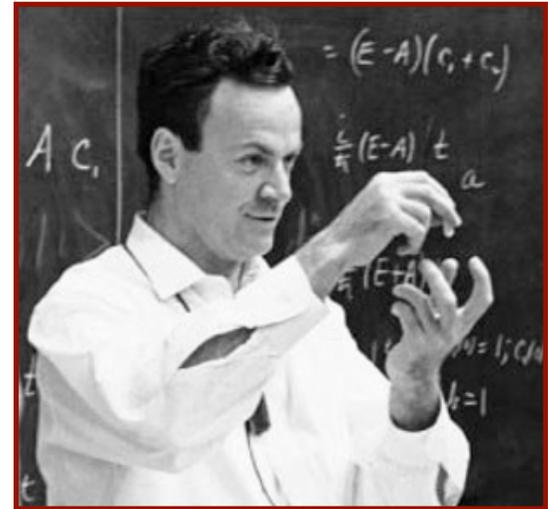
$$e^{-\beta \hat{H}} = e^{-E / k_B T}$$

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

Density matrix definition:

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

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



Density matrix properties:

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

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

Imaginary time path integrals $\tau = it$

(used for many simulations)

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

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

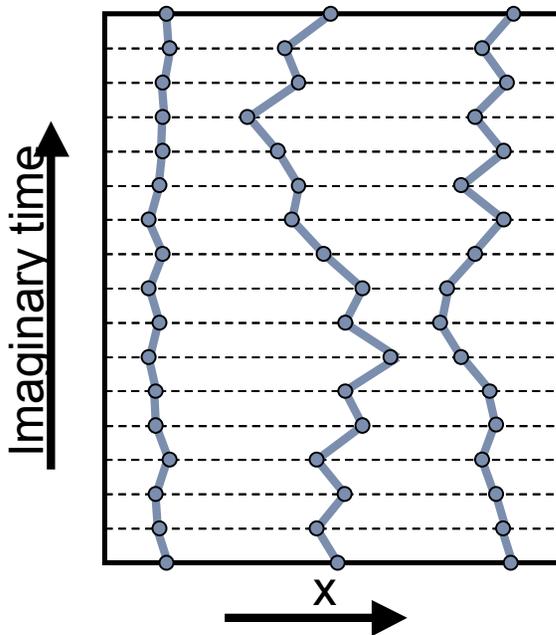
$$e^{-\beta \hat{H}} = e^{-E / k_B T}$$

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

Density matrix definition:

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

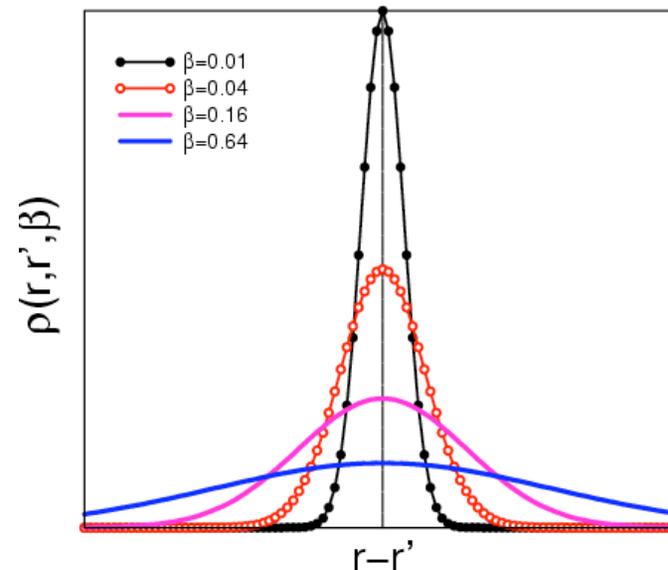
$$\rho(R, R', \beta) = \sum_S e^{-\beta E_S} \Psi_S^*(R) \Psi_S(R')$$



Free particle density matrix:

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

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



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

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

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:

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

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

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:

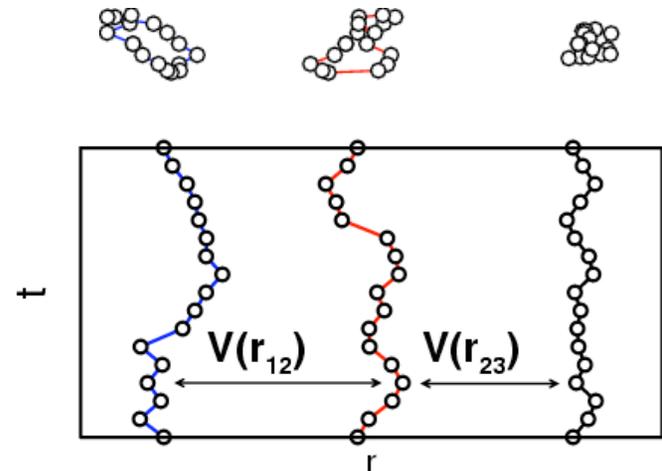
$$\langle R | \hat{\rho} | R' \rangle = \langle R | (e^{-\tau\hat{H}})^M | R' \rangle = \int dR_1 \dots \int dR_{M-1} \langle R | e^{-\tau\hat{H}} | R_1 \rangle \langle R_1 | e^{-\tau\hat{H}} | R_2 \rangle \dots \langle R_{M-1} | e^{-\tau\hat{H}} | R' \rangle$$

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

Path integral and primitive action **S** :

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

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



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:

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

Analogy to groundstate QMC:

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

PIMC literature:

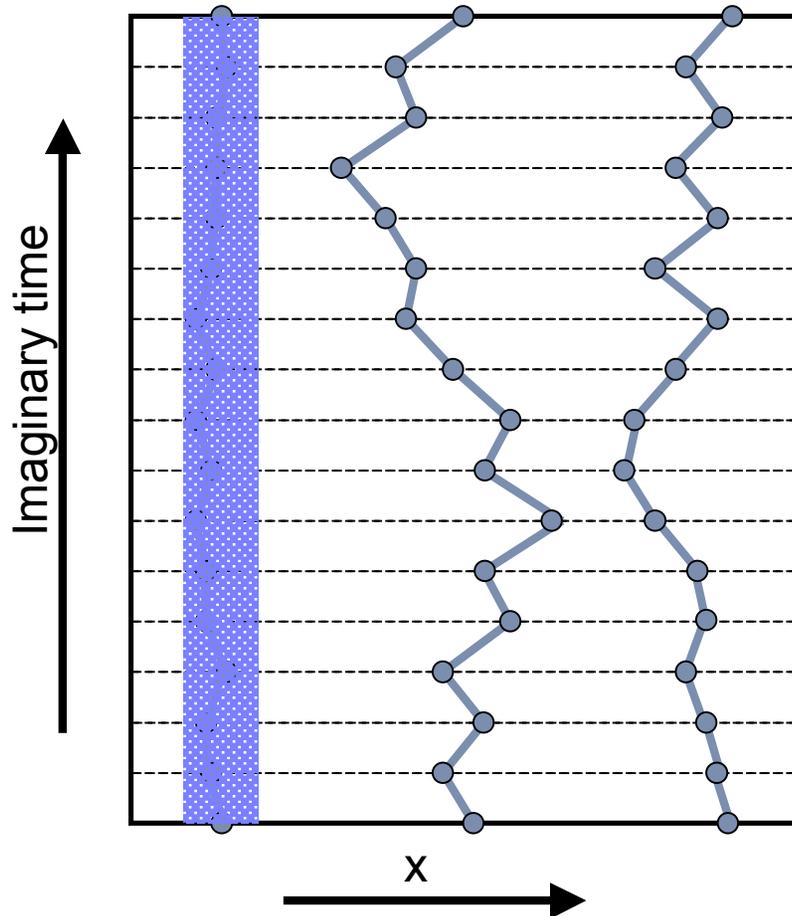
D. Ceperley, *Rev. Mod. Phys.* **67** (1995) 279.

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

B. Militzer, PhD thesis, see <http://militzer.gl.ciw.edu>

Write your own PIMC code

What is needed to start?



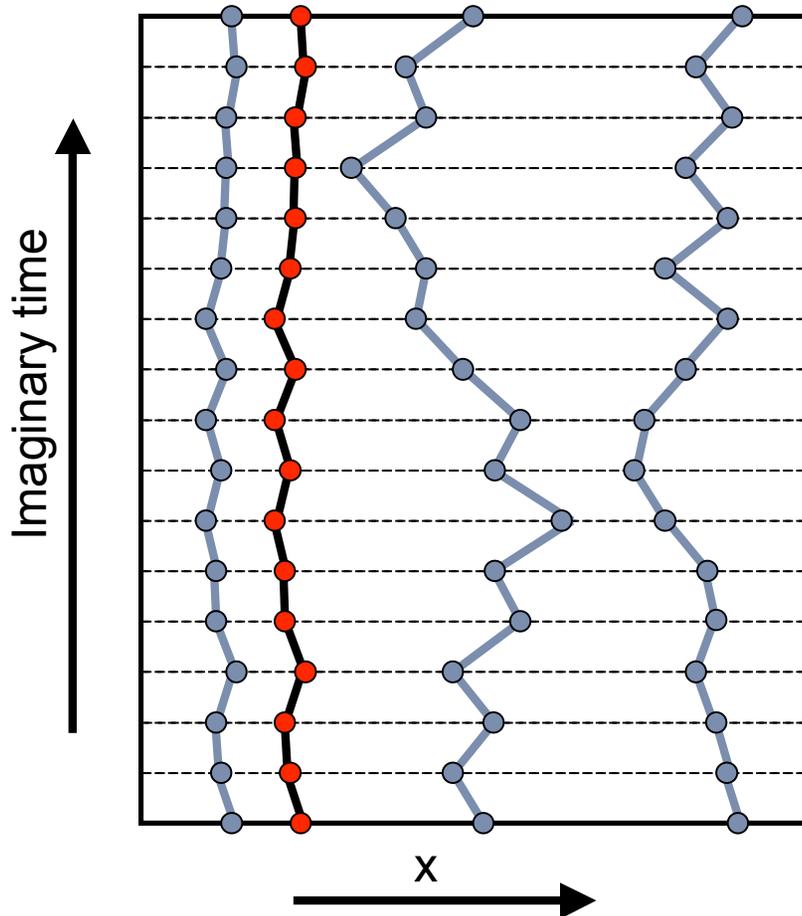
- 1) Initialize the paths as classical particle on a lattice.
- 2) Pick one **“bead”** and sample **new position**
- 3) Compute the difference in *kinetic and potential action*
- 4) Accept or reject based on

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

- 5) Try a **“classical” move** - shift a polymer as a whole.

Write your own PIMC code

What is needed to start?



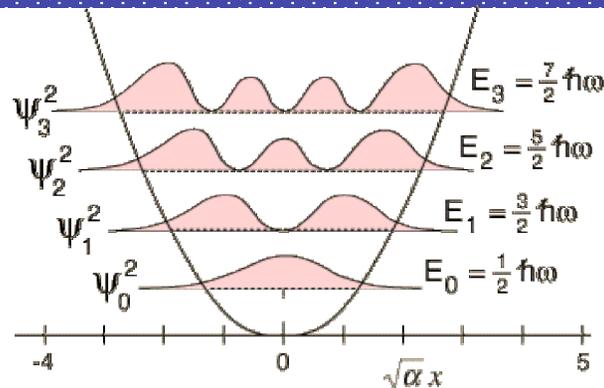
- 1) Initialize the paths as classical particle on a lattice.
- 2) Pick one **“bead”** and sample **new position**
- 3) Compute the difference in *kinetic and potential action*
- 4) Accept or reject based on

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

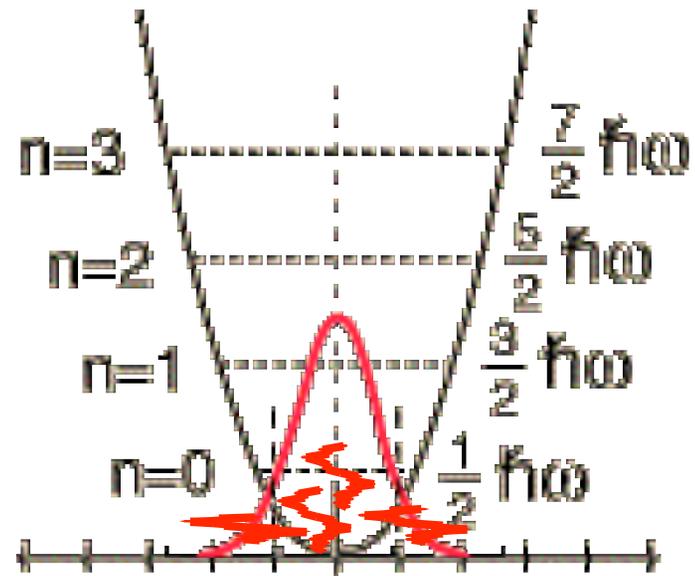
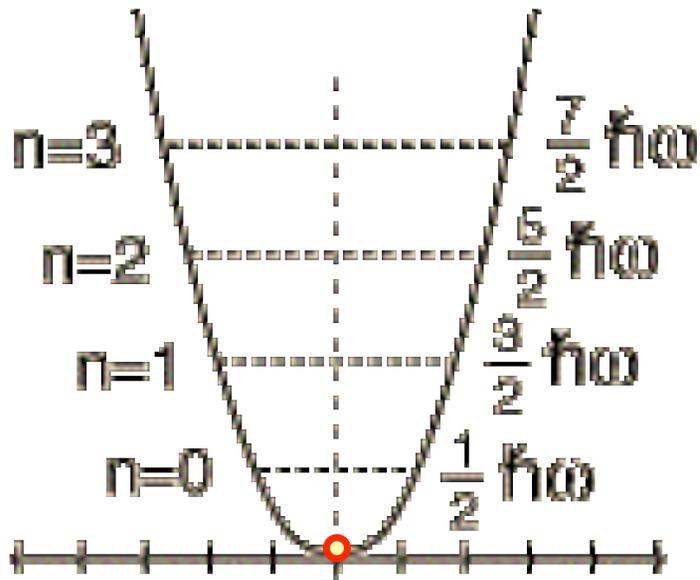
- 5) Try a **“classical” move** - shift a polymer as a whole.
- 6) Compute *potential action* and accept or reject.
- 7) Go back to step 2).

Example: PIMC for the harmonic oscillator

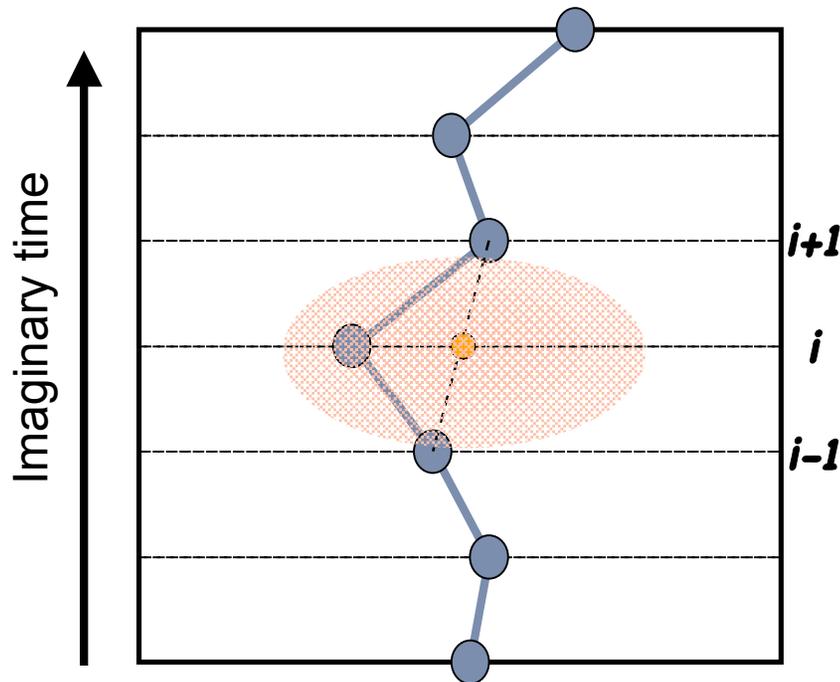
Classical simulation
for $T \rightarrow 0$
Gives the classical
ground state $E_0=0$



PIMC simulation for
 $T \rightarrow 0$ give the correct
qm ground state
energy $E_0 = \frac{1}{2} \hbar\omega$



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 $P(r_i)$.

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

Building a Browning Bridge

Method 1: Levy Flights

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

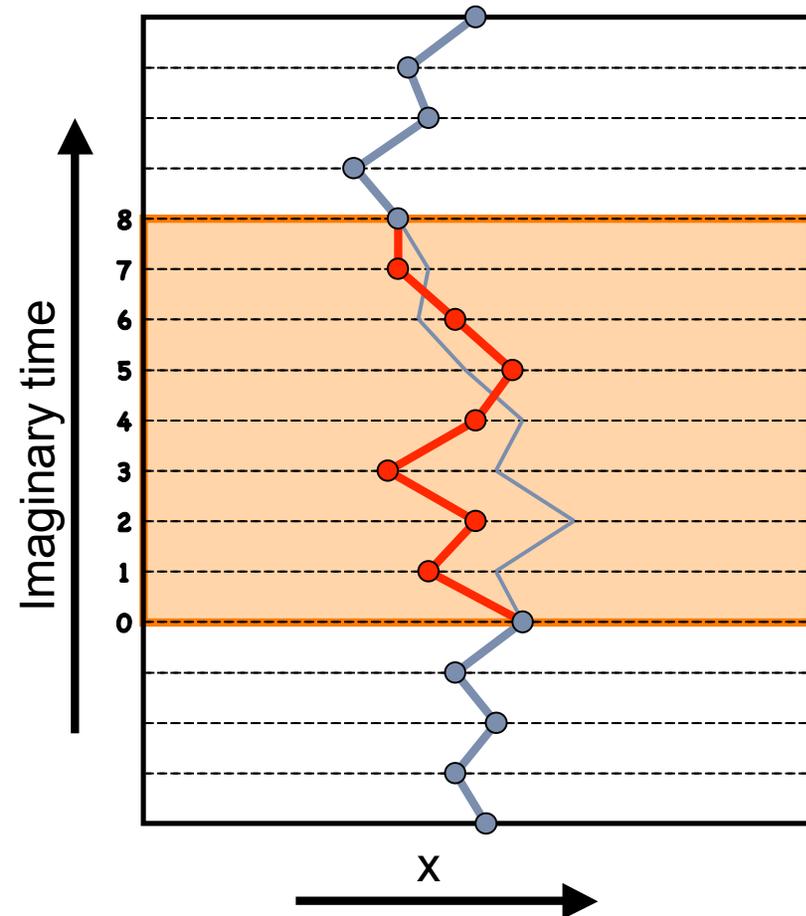
Step 4: Sample the fourth point r_4

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 based on the **potential action** since it was not considered in the Levy flight generation.



Building a Browning Bridge

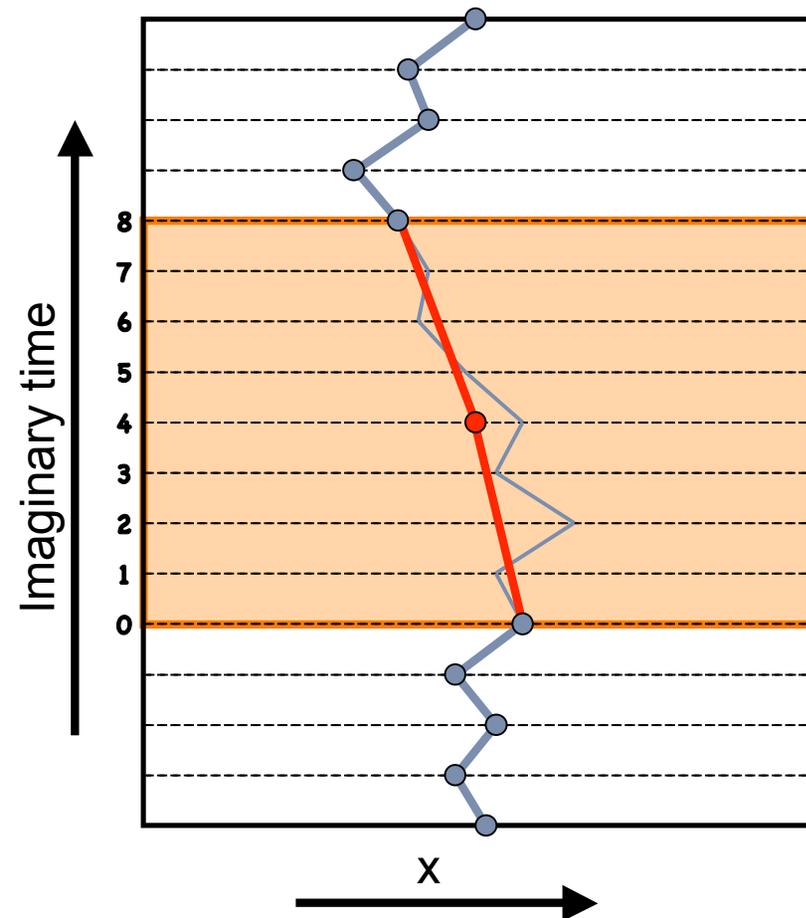
Method 2: Bisection

Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window

Step 1: Sample the first point \vec{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

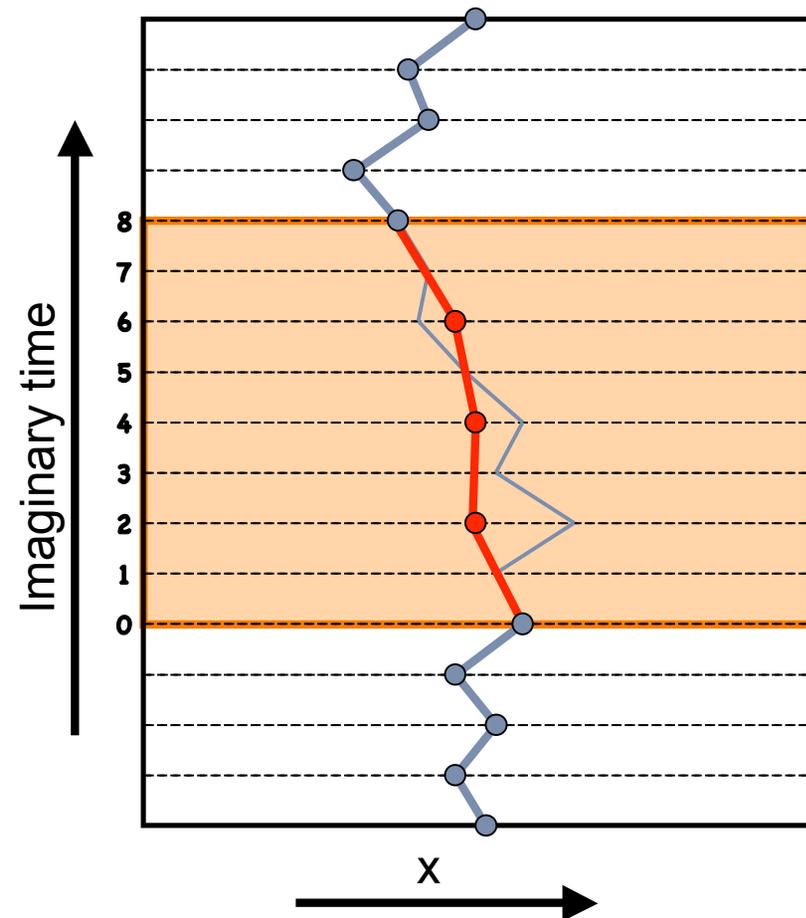
Multi-slice moves are more efficient!

Step 0: Pick an imaginary time window

Step 1: Sample the first point r_4

Step 2: Sample points r_2 and r_6 :

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



Building a Browning Bridge

Method 2: Bisection

Multi-slice moves are more efficient!

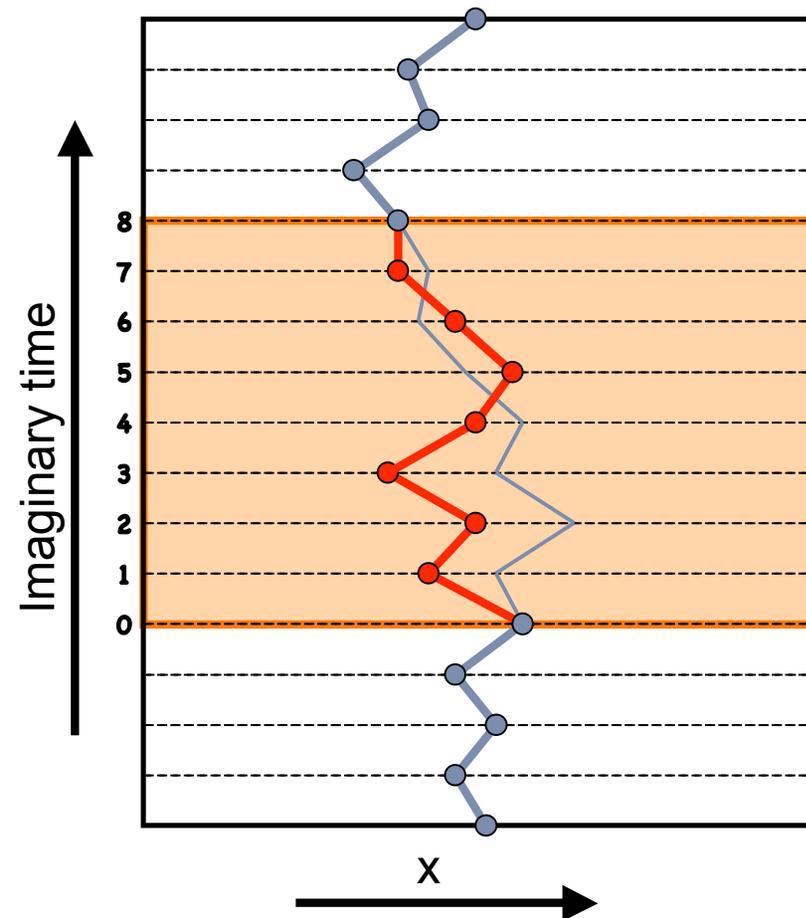
Step 0: Pick an imaginary time window

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.



Making a better action: Pair action method

$$\langle R | \hat{\rho} | R' \rangle = \oint_{R \rightarrow R'} dR_t e^{-S[R_t]} \quad S[R_t] = \sum_{i=1}^M \frac{(R_{i+1} - R_i)^2}{4\lambda\tau} + \frac{\tau}{2} [V(R_i) + V(R_{i+1})]$$

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-diagonal elements at once. Disadvantage: Integration is performed on a grid. Grid error must be carefully controlled.

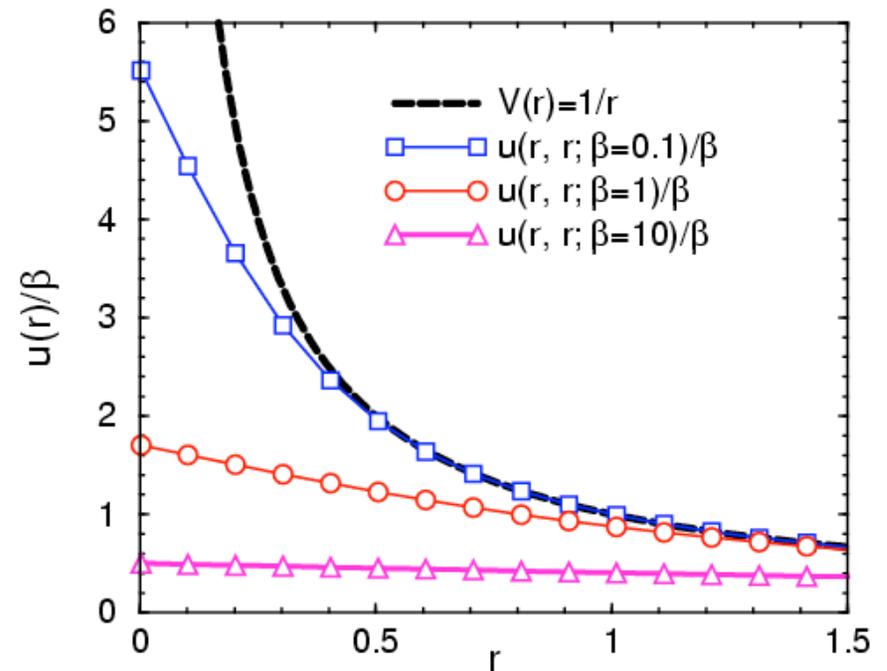
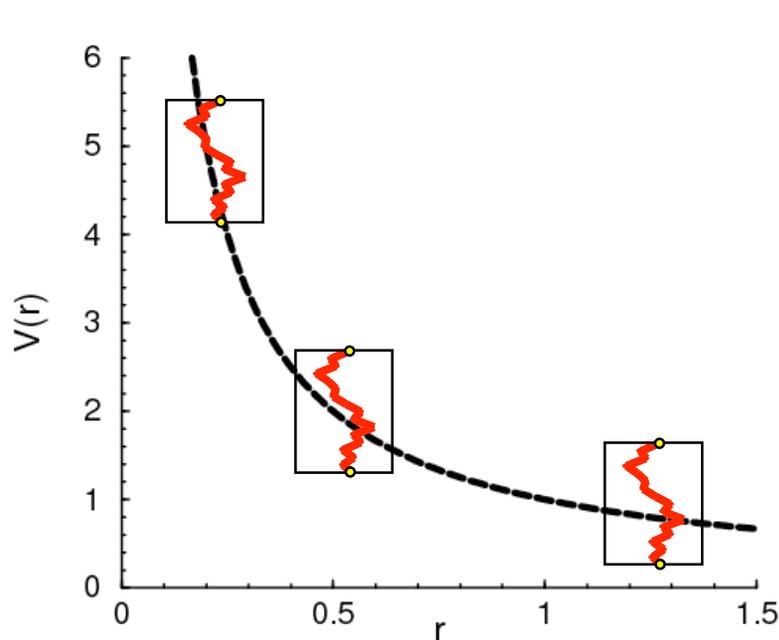
(3) Feynman-Kac formula:

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 brownian 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 brownian bridge. Feynman-Kac formula:

$$\rho(r, r', \beta) \equiv \exp[-S(r, r', \beta)] \equiv \exp[-(S_0 + S_I)] = \rho_0(r, r', \beta) \left\langle \exp\left[-\int dt V[r(t)]\right] \right\rangle_{BB}$$



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 performed 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.

