2.3 Path integral formalism

2.3.1 Path integral representation of time evolution amplitudes

- developed by R.P. Feynman in the 1940s
- consider transition elements of a particle between coordinates x_a and x_b (1D),

$$(x_b t_b | x_a t_a) = \langle x_b | \hat{U}(t_b, t_a) | x_a \rangle \,, \quad \underbrace{t_b > t_a}_{\text{causality!}}$$

with $\hat{U}(t_b, t_a)$ being the time evolution operator.

Definition of time evolution operator

$$|\Psi(t_b)\rangle = \underbrace{e^{-\frac{i}{\hbar}(t_b - t_a)\hat{H}}}_{\hat{U}(t_b,t_a)} |\Psi(t_a)\rangle$$

$\Rightarrow$ satisfies the differential equation (TD Schrödinger equation)

$$i\hbar \partial_{t_b} \hat{U}(t_b, t_a) = \hat{H}\hat{U}(t_b, t_a)$$

Consider inverse evolution: interchange order of t_b, t_a

$$\hat{U}^{-1}(t_b, t_a) = e^{\frac{i}{\hbar}(t_b - t_a)\hat{H}} = \hat{U}(t_a, t_b)$$

- $\hat{U}$ is unitary operator satisfying $\hat{U}^\dagger = \hat{U}^{-1}$
$\Rightarrow \hat{U}^\dagger(t_b, t_a) = e^{\frac{i}{\hbar}(t_b - t_a)\hat{H}^\dagger} = \hat{U}^{-1}(t_b, t_a)$

General case: time-dependent Hamiltonian $\hat{H} = \hat{H}(t)$

$$\hat{U}(t_b, t_a) = \hat{T} \exp\left\{ -\frac{i}{\hbar} \int_{t_a}^{t_b} dt \hat{H}(t) \right\}$$

$\hat{T}$ time-ordering operator
- if $\hat{H}$ does not depend on t, the integral is trivial, and $\hat{T}$ is superfluous

Fundamental composition law (semigroup property):

$$\hat{U}(t_b, t_a) = \hat{U}(t_b, t')\hat{U}(t', t_a), \quad t' \in (t_a, t_b)$$

Proof for time-independent hamiltonian trivial. Proof for time-dependent case:

$$\hat{T}\left[\exp\left\{ -\frac{i}{\hbar} \int_{t'}^{t_b} \hat{H}(t)\, dt \right\} \hat{T} \exp\left\{ -\frac{i}{\hbar} \int_{t_a}^{t'} \hat{H}(t)\, dt \right\} \right]$$

$$= \hat{T} \exp\left\{ -\frac{i}{\hbar} \int_{t_a}^{t_b} \hat{H}(t) dt \right\} = \hat{U}(t_b, t_a)$$

2.3.2 Introduction of "time slices"

Composition law: Transition from t_a to t_b can be "sliced" into a large number $(N+1)$ of small time steps, each slice having thickness $\epsilon = t_n - t_{n-1} = \frac{t_b - t_a}{N+1} > 0$

$$(x_b t_b | x_a t_a) = \langle x_b | \hat{U}(t_b, t_N)\hat{U}(t_N, t_{N-1})...\hat{U}(t_1, t_a) | x_a \rangle$$

- Insert $\hat{1} = \int dx_n |x_n\rangle \langle x_n|$ between all pairs of $\hat{U}(..)$

$$(x_b t_b | x_a t_a) = \Pi_{n=1}^{N} \left[\int dx_n \right] \Pi_{n=1}^{N+1} (x_n t_n | x_{n-1} t_{n-1})$$

with the limits $x_b = x_{N+1}$, $x_a = x_0$, $t_b = t_{N+1}$, $t_a = t_0$.

Note that

$$(x_n t_n | x_{n-1} t_{n-1}) = \langle x_n | e^{i\epsilon \hat{H}(t_n)/\hbar} | x_{n-1} \rangle$$

Use notation $\hat{H} = \hat{H}(\hat{p}, \hat{x}, t)$.

Let's assume $\hat{H}$ allows for the following decomposition into a kinetic ($\hat{T}$) and potential ($\hat{V}$) part:

$$\hat{H}(\hat{p}, \hat{x}, t) = \hat{T}(\hat{p}, t) + \hat{V}(\hat{x}, t)$$

time evolution operator for a small slice ϵ

$$e^{-\frac{i}{\hbar}\epsilon \hat{H}} = e^{-\frac{i}{\hbar}\epsilon(\hat{T}+\hat{V})}$$

This can be factorized as (Baker-Campbell-Hausdorff formula)

$$e^{-\frac{i}{\hbar}\epsilon(\hat{T}+\hat{V})} = \underbrace{e^{-\frac{i}{\hbar}\epsilon \hat{V}} e^{-\frac{i}{\hbar}\epsilon \hat{T}}}_{\text{"primitive"}} \underbrace{e^{-\frac{i}{\hbar^2}\epsilon^2 \hat{X}}}_{\sim \epsilon^2}$$

with $\hat{X}$ being given by the expansion

$$\hat{X} = \frac{i}{2}[\hat{V}, \hat{T}] - \frac{\epsilon}{\hbar}\left(\frac{1}{6}[\hat{V}, [\hat{V}, \hat{T}]] - \frac{1}{3}[[\hat{V}, \hat{T}], \hat{T}] \right) + \mathcal{O}(\epsilon^2)$$

additional terms contain higher order commutators of $\hat{T}, \hat{V}$ and are of order ϵ^4 in the full expression

Limit of large N/small ϵ

$\hat{X}$ is suppressed by a factor $\epsilon^2 \sim \frac{1}{N^2}$. In this limit this can be ignored, resulting in a *semi-classical expression:*

- evaluation of transition matrix elements becomes possible:

$$\langle x_n | e^{-\frac{i}{\hbar}\epsilon \hat{H}(\hat{p}, \hat{x}, t)} | x_{n-1} \rangle \approx \int dx \langle x_n | e^{-\frac{i}{\hbar}\epsilon V(\hat{x}, t_n)} | x \rangle \langle x | e^{-\frac{i}{\hbar}\epsilon \hat{T}(\hat{p}, t_n)} | x_{n-1} \rangle$$

$$= \int dx \, \langle x_n | \, e^{-\frac{i}{\hbar}\epsilon V(x,t_n)} \, |x\rangle \int_{-\infty}^{\infty} \frac{dp_n}{2\pi\hbar} e^{i\frac{p_n}{\hbar}(x-x_{n-1})} e^{-i\epsilon T(p_n,t_n)/\hbar}$$

evaluate the local matrix elements using $\langle x_n|x\rangle = \delta(x_n - x)$,

$$\langle x_n | \, e^{-\frac{i}{\hbar}\epsilon V(\hat{x},t_n)} \, |x\rangle = \delta(x_n - x) e^{-\frac{i\epsilon}{\hbar}V(x_n,t_n)}$$

$\Rightarrow \langle x_n | \, e^{-\frac{i}{\hbar}\epsilon \hat{H}(\hat{x},\hat{p},t)} \, |x_{n-1}\rangle$

$$\approx \int_{-\infty}^{\infty} \frac{dp_n}{2\pi\hbar} \exp\left\{ \frac{i}{\hbar} p_n (x_n - x_{n-1}) - i\epsilon [T(p_n,t_n) + V(x_n,t_n)] \right\}$$

Inserting this into the original transition element yields Feynman's path integral formula:

$$(x_b t_b | x_a t_a) \approx \prod_{n=1}^{N} \left[\int dx_n \right] \prod_{n=1}^{N+1} \left[\int_0^{\infty} \frac{dp_n}{2\pi\hbar} \right] \exp\left\{ \frac{i}{\hbar} S^{(N)} \right\},$$

with $S^{(N)}$ being the action

$$S^{(N)} = \sum_{n=1}^{N+1} [p_n (x_n - x_{n-1}) - \epsilon H(p_n, x_n, t_n)] \,, \tag{2.16}$$

where all "paths" contribute according to the action term, $\exp\big(\frac{i}{\hbar} S^{(N)}\big)$.

2.3.3 Connection to the Schrödinger equation

The transition amplitude can be written as

$$(x_b t_b | x_a t_a) \approx \int dx_n (x_b t_b | x_n t_n)(x_n t_n | x_a t_a), \,,$$

with

$$(x_b t_b | x_n t_n) \approx \int_{-\infty}^{\infty} \frac{dp_n}{2\pi\hbar} e^{\frac{i}{\hbar}(p_b(x_b - x_n) - \epsilon H(p_b, x_n, t_n))} \,.$$

Use trick: momentum p_b inside of the integral can be generated by a differential operator $\hat{p}_b = \frac{\hbar}{i}\partial_{x_b}$ outside the integral (same applies for any function of p_b). Move hamiltonian in front of integral:

$$(x_b t_b | x_a t_a) \approx e^{-i\frac{\epsilon}{\hbar}H(-i\hbar\partial_{x_b}, x_b, t_b)} \int_{-\infty}^{\infty} \frac{dp_b}{2\pi\hbar} e^{\frac{i}{\hbar}p_b(x_b - x_n)} = e^{-\frac{i\epsilon}{\hbar}H(-i\hbar\partial_{x_b}, x_b, t_b)} \delta(x_b - x_n)$$

$$\Rightarrow (x_b, t_b|x_a, t_a) \approx e^{-i\epsilon/\hbar H(-i\hbar\partial x_b, x_b, t_b)}(x_b, t_b - \epsilon|x_a t_a)$$

This is equivalent to

$$\frac{1}{\epsilon}[(x_b t_b + \epsilon|x_a t_a) - (x_b t_b|x_a t_a)] \approx 1/\epsilon[e^{-i\epsilon H(-i\hbar\partial_{x_b}, x_b, t_b+\epsilon)} - 1](x_b t_b, x_a t_a)$$

Take $\epsilon \to 0$ limit, results in differential equation:

$$i\hbar\partial_{t_b}(x_b t_b|x_a t_a) = H(-i\hbar\partial_{x_b}, x_b, t_b)(x_b t_b|x_a t_a)$$

$\Rightarrow$ Schrödinger equation of operator quantum mechanics

2.3.4 The continuous time limit

Let us take the limit of a time slice $\epsilon = \frac{t_b - t_a}{1+N} \to 0$, with $N \to \infty$

then the Trotter formula

$$e^{-\frac{i}{\hbar}(t_b - t_a)\hat{H}} = \lim_{N\to\infty}(e^{-\frac{i\epsilon}{\hbar}\hat{V}}e^{-\frac{i\epsilon}{\hbar}\hat{T}})$$

$\Rightarrow$ with the "primitive factorization"

$$e^{-\frac{i\epsilon}{\hbar}(T+V)} \approx e^{-\frac{i\epsilon}{\hbar}V}e^{-\frac{i\epsilon}{\hbar}\hat{T}}$$

becomes exact, for $N \to \infty$, $\approx \to =$
But: Trotter formula only holds for potentials V that are *bounded from below*

Example: Coulomb repulsion between two electrons $V(r) = \frac{|e|^2}{r}$, for $r \to 0$, $V(r) \to \infty$, observe simple behaviour
In particular, the UEG is directly accessible to the path integral formalism.

Counter-example: Coulomb attraction between electron and proton

$$V(r) = -\frac{|e|^2}{r}, \quad \lim_{r\to 0} V(r) = -\infty$$

Therefore, atomic systems require additional considerations, like quantum pair potentials (e.g. Kelbg or Deutsch), or the exact solution of the two-body problem where the negative divergence is removed. $\to$ See text book by Hagen Kleinert, *Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets*

Continuum limit of the action

The sum in $S^{(N)}$ in Eq. (2.16) tends towards an integral:

$$S^{(N)} \to S[p, x] = \int_{t_b}^{t_a} dt\, [p(t)\dot{x}(t) - H(p(t), x(t), t)] \equiv \int_{t_b}^{t_a} dt\, L(t, x, \dot{x})\,. \tag{2.17}$$

This is exactly the classical expression.

The quantum case is obtained from the limit of infinitely many integrals: this yields the *path integral (functional integral)*

$$\lim_{N\Rightarrow\infty}\prod_{n=1}^{N}\left[\int_{-\infty}^{\infty}dx_n\right]\prod_{n=1}^{N+1}\left[\int_{-\infty}^{\infty}\frac{dp_n}{2\pi\hbar}\right]\equiv\int_{x(t_a)=x_a}^{x(t_b)=x_b}\mathcal{D}x\int\frac{\mathcal{D}p}{2\pi\hbar}$$

Note: there is always one more p-integral than x-integral, $\mathcal{D}x$, $\mathcal{D}p$
- x_0, x_{N+1} are fixed $\rightarrow n = 1, \dots, N$ integrals
- each pair (x_n, x_{n-1}) has one p_n-integral for $n = 1, \dots, N+1$
Write transition amplitude in short form:

$$(x_b t_b|x_a t_a)=\int_{x(t_a)}^{x(t_b)}\mathcal{D}x\int\frac{\mathcal{D}p}{2\pi\hbar}\,e^{\frac{i}{\hbar}S[p,x]}$$

- integration over all paths corresponds to *summation over all histories (trajectories in 6N-dimensional phase space) along which a physical system can evolve*
- the exponential $e^{\frac{i}{\hbar}S[p,x]}$ is heuristically analogous to Boltzmann weight
- a phase factor is assigned to each possible history
$\Rightarrow$ total amplitude for going from x_a, t_a to x_b, t_b is obtained by adding the phase factors of all possible trajectories

$$(x_b, t_b|x_a, t_a)=\sum_{\text{histories},(x_a,t_a)\to(x_b,t_b)}e^{\frac{i}{\hbar}S[p,x]}\,.$$

So this corresponds to a quantum superposition (interference) of all possible paths. In contrast to the classical case, Eq. (2.17), there is not only a single trajectory that follows from the variational principle.
Note that this derivation can be repeated for an N-particle system with interactions, nothing will change qualitatively.

2.4 Path integral Monte Carlo (PIMC)

Goal: Simulate N spin-polarized ($N = N_\uparrow, N_\downarrow = 0$) electrons in the canonical ensemble (N, V, T are fixed)
3D: cubic box, $V = L^3$
All thermodynamic properties can be derived from the partition function Z

$$Z = \mathrm{Tr}\,\hat{\rho}$$

density operator, canonical:

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

inverse temperature

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

PIMC: evaluate the trace of Z in coordinate space

2.4.1 Path integral representation of the partition function

Let's for now consider distinguishable particles ("boltzmannons")

$$Z = \int d\mathbf{R}\, \langle \mathbf{R}| \, e^{-\beta \hat{H}} \, |\mathbf{R}\rangle \,, \quad \mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_N)^T$$

$\mathbf{r}_i, i = 1, \dots, N$: coordinate vector of an individual particle
Problem: Matrix elements of $\hat{\rho}$ cannot readily be evaluated, as kinetic contribution $\hat{T}$ and potential contribution $\hat{V}$ to the full Hamiltonian, $\hat{H} = \hat{T} + \hat{V}$, do not commute:

$$e^{-\beta \hat{H}} = e^{-\beta \hat{V}} e^{-\beta \hat{T}} + \mathcal{O}(\beta^2)$$

(Baker-Campbell-Hausdorff formula)
Primitive factorization: $e^{-\beta \hat{H}} \approx e^{-\beta V} e^{-\beta T}$ becomes increasingly inaccurate when T is decreased (β is increased), and then neglects "quantum effects". This means, here one over temperature plays the role of time in the path integral approach to quantum dynamics, cf. Sec. 2.3.

Solution: use (semi-)group property of $\hat{\rho}$:

$$\hat{\rho} = e^{-\beta H} = \prod_{\alpha=0}^{P-1} e^{-\epsilon \hat{H}}, \quad \text{with } \epsilon = \frac{\beta}{P}$$

Each factor now has a P times higher temperature than the original system.

$$\Rightarrow Z = \int d\mathbf{R} \left\langle \mathbf{R} \middle| \prod_{\alpha=0}^{P-1} \underbrace{e^{-\epsilon H}}_{\text{insert P-1 unities of the form } 1=\int dR_\alpha |R_\alpha\rangle\langle R_\alpha|} \middle| \mathbf{R} \right\rangle$$

$$= \int dR_0 \dots dR_{P-1} \, \langle R_0| \, e^{-\epsilon H} \, |R_1\rangle \dots |R_{P-1}\rangle \, \langle R_{P-1}| \, e^{-\epsilon H} \, |R_P\rangle \,,$$

with $R_0 = R_P = R$.

- The partition function was originally given as a trace over low-T matrix elements, now re-cast as trace over product of P matrix elements at $\tilde{T} = P \cdot T$ (high T)

$$Z = \int \prod_{\alpha=0}^{P-1} d\mathbf{R}_\alpha \, \rho(\mathbf{R}_\alpha, \mathbf{R}_{\alpha+1}; \epsilon) \tag{2.18}$$

- now we can use a high-T approximation to evaluate the $\rho(R_\alpha, R_{\alpha+1}; \epsilon)$

A note on "imaginary-time" path-integrals

in TD equilibrium the hamiltonian $\hat{H}$ does not depend on time t, therefore, the time evolution operator

$$\hat{U}(t_2, t_1) = \exp\left\{-\frac{i}{\hbar}\hat{H}(t_2 - t_1)\right\}$$

only depends on $t = t_2 - t_1$:

$$\hat{U}(t) = \exp\left\{-\frac{i}{\hbar}\hat{H}t\right\},$$

- introduce formally an imaginary-time argument $\tau = -i\hbar\beta$.

Calculation of ensemble averages using the canonical density operator ρ is equivalent to a "propagation" in the "imaginary time" τ:

$$\hat{U}(\tau) = \exp\left\{-\frac{i}{\hbar}\hat{H}\tau\right\} = \exp\left\{-\frac{i}{\hbar}\hat{H}(-i\hbar\beta)\right\} = \exp\left\{-\beta\hat{H}\right\}.$$

For the partition function in PIMC: discretization corresponds to the integral over all closed paths in the imaginary time from $\tau = 0$ to $\tau = -i\hbar\beta$, and each factor $e^{-\epsilon H}$ corresponds to the propagator of one designated imaginary-time step.
Conventions:

$$\tilde{\tau} \in [0, \beta], \quad \tilde{\tau} = \frac{\tau}{-i\hbar}$$

PIMC configuration

$$Z = \int d\mathbf{X}\, W(\mathbf{X}), \quad \mathbf{X} = \{\mathbf{R}_0, \ldots, \mathbf{R}_{P-1}\}^T$$

$3PN$-dimensional integration variable, "configuration" (microstate) with weight

$$W(\mathbf{X}) = \prod_{\alpha=0}^{P-1} \rho(\mathbf{R}_\alpha, \mathbf{R}_{\alpha+1}; \epsilon)$$

of configuration $\mathbf{X}$, contribution to the partition function Z

2.4.2 PIMC in the "primitive" approximation

consider one high-temperature factor and use the primitive factorization:

$$\rho(\mathbf{R}_1, \mathbf{R}_2; \epsilon) \approx \langle \mathbf{R}_1 | \, e^{-\epsilon T} e^{-\epsilon V} \, | \mathbf{R}_2 \rangle$$

insert identity:

$$= \int d\mathbf{R}' \, \langle \mathbf{R}_1 | \, e^{-\epsilon T} \, | \mathbf{R}' \rangle \langle \mathbf{R}' | \, e^{-\epsilon V} \, | \mathbf{R}_2 \rangle$$

$$= \int d\mathbf{R}' \quad \underbrace{\rho_0(\mathbf{R}_1, \mathbf{R}'; \epsilon)}_{\text{ideal, noninteracting density matrix}} \quad \underbrace{\rho_{pot}(\mathbf{R}', \mathbf{R}_2; \epsilon)}_{\text{potential (interaction) contribution}}$$

Explicit result for the matrix element of the kinetic term (hint: introduce momentum eigenstates via $\hat{1} = \int d\mathbf{p}|\mathbf{p}\rangle\langle\mathbf{p}|$):

$$\rho_0(\mathbf{R}_1, \mathbf{R}_2; \epsilon) = \left(\frac{m}{2\pi\epsilon\hbar^2}\right)^{3N/2} \exp\left\{-\frac{m}{2\epsilon\hbar^2}(\mathbf{R}_1 - \mathbf{R}_2)^2\right\}$$

The pre-factor is the thermal (de Broglie) wave length for the high temperature (1 time slice):

$$\lambda_\epsilon = \sqrt{\frac{2\pi\hbar^2\epsilon}{m}} = \frac{h}{\sqrt{2\pi m k_B\,(PT)}}$$

Kinetic term:
now insert λ_ϵ and explicitly write the components of $\mathbf{R}$:

$$\rho_0(\mathbf{R}_1, \mathbf{R}_2; \epsilon) = \frac{1}{\lambda_\epsilon^{3N}} \exp\left\{-\frac{\pi}{\lambda_\epsilon^2}(\mathbf{R}_1 - \mathbf{R}_2)\right\} = \prod_{i=1}^{N}\prod_{d=1}^{3} \frac{1}{\lambda_\epsilon} \exp\left\{-\frac{\pi}{\lambda_\epsilon^2}(x_{i,1}^d - x_{i,2}^d)^2\right\}$$

have $3N$ 1d factors where $x_{i,1}^d$ denotes the coordinate in dimension d of particle i on slice 1. Thus, the N-particle free density matrix is a product of Gaussians.

recall the generic form of a 1d Gaussian and identify the variance in our case:

$$f(x; \sigma, \mu) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left\{-\frac{(x-\mu)^2}{2\sigma^2}\right\}$$

$$\frac{1}{2\epsilon^2} = \frac{\pi}{\lambda_\epsilon^2} \Rightarrow \sigma = \frac{\lambda_\epsilon}{\sqrt{2\pi}}$$

This means, the variance is proportional to the thermal wavelength of a single imaginary time slice, ϵ.
Classical limit: From this the classical limit is clear: this corresponds to the high-temperature limit where $\lambda \to 0$, resulting in a straight path. In other words, the kinetic energy becomes a diagonal matrix (delta function) and the intermediate factors can be integrated out.

Potential term: The potential energy is a function of the coordinates only. Thus, in coordinate representation, it is given by a diagonal matrix:

$$\rho_{pot}(\mathbf{R}_1, \mathbf{R}'; \epsilon) = \langle\mathbf{R}_1|\, e^{-\epsilon V(R_1)}\, |\mathbf{R}'\rangle = e^{-\epsilon V(R_1)}\delta(R_1 - R')$$

with a $3NP$-dimensional delta function
here we defined the total potential energy:

$$e^{-\epsilon V(R_1)} = \exp\left\{-\epsilon\left(\sum_{i=1}^{N} V_{ext}(\mathbf{r}_{i,1}) + \frac{1}{2}\sum_{i\neq k}^{N} W(\mathbf{r}_{i,1}, \mathbf{r}_{k,2})\right)\right\}$$

$$\hat{V} = \underbrace{\hat{V}_{ext}}_{\text{“external” single-particle potential}} + \underbrace{\hat{W}}_{\text{pair interaction, e.g. Coulomb repulsion}}$$

The result for the total density matrix on a single time slice is now

$$\rho(R_1, R_2; \epsilon) = \int dR' \rho_0(R_1, R'; \epsilon) e^{-\epsilon V(\mathbf{R}_1)} \delta(R_1 - R') = \rho_0(R_1, R_2, \epsilon) e^{-\epsilon V(R_1)} \tag{2.19}$$

2.4.3 Result for the PIMC partition function. Discussion

Inserting the results (2.19) into the partition function (2.18) we obtain:

$$Z = \int dR_0 \dots dR_{P-1} \prod_{\alpha=0}^{P-1} \frac{1}{\lambda_\epsilon^{3N}} \exp\left\{ -\frac{\pi}{\lambda_\epsilon^2} \sum_{i=1}^{N} (r_{i,\alpha} - r_{i,\alpha+1})^2 - \epsilon V(\mathbf{R}_\alpha) \right\} \equiv \int d\mathbf{X}\, W(\mathbf{X}) \,,$$

where $\mathbf{X}$ is given by closed N-particle paths in the imaginary time

Example and discussion
Abbildung: N=2, P=4, closed paths
- beads from different particles on the same time slice interact via pair potential W
- beads on adjacent slices from the same particle interact via “harmonic” spring potential due to the free-particle density matrix (“classical isomorphism”)
- map complicated quantum many-body system of interest onto an effective classical system of interacting ring polymers
- the extension of the paths is mostly proportional to the thermal wavelength
- beads on adjacent slices are within λ_ϵ
- the full path has an extension $\sim \lambda_\beta$
high T: classical limit $\lim_{\beta \to 0} \lambda_\beta = 0$
low T: extension of the paths increases, although this is typically bounded by the pair interaction
Note: there exist other observable that are connected to off-diagonal matrix elements of ρ. In that case the path is no closed. Examples are transition probabilities or the Matsubara Green function.

2.4.4 A note on higher-order factorization of $\hat{\rho}$

- Primitive approximation gives Z and $W(\mathbf{X})$ converging as $\mathcal{O}(\frac{1}{P^2})$
- This might be too slow/inefficient at low T (long propagation in τ) and $P \sim 10^3 - 10^9$ could be required
$\Rightarrow$ extremely high-dimensional integrals, can be evaluated with MC methods
$\Rightarrow$ computation time increases as $\sim P$

Idea: include at least some of the commutator terms from the Baker-Campbell-Hausdorff formula [Chin/Chen 2002]

$$e^{-\epsilon H} \approx e^{-V_1 \epsilon W_{a_1}} e^{-t_1 \epsilon K} e^{-v_2 \epsilon W_{1-2a_1}} e^{-t_1 \epsilon K} e^{-v_1 \epsilon W_{a_2}} e^{-2t_a \epsilon K}$$

$$[[V,K],V] = \frac{\hbar^2}{m} \sum_{i=1} |\mathbf{F}_i|^2$$

$\mathbf{F}_i$: full force acting on particle i
modified “effective” potentials including force terms

$$W_{a_1} = V + \frac{u_0}{v_1} a_1 \epsilon^2 \left(\frac{\hbar^2}{m} \sum_{i=1}^{N} |F_i|^2 \right)$$

v_1, v_2, u_0, t_1, t_0 are inter-dependent, two of them (e.g. t_0 and v_1), can be freely chosen
Abbildung: intermediate time slices 3K-term in the factorization → 3 time slices for each time step ϵ
larger computation cost for each step compared to the primitive approximation, but convergence scales as $\mathcal{O}(\frac{1}{P^4})$
→ fourth-order propagator in the imaginary time
Sakkos / Casulleras / Boronat, J. Chem. Phys. 130 (2009)
Application to Fermi systems: Dornheim, Groth, Filinov, Bonitz, New J. Phys. 17 (2015)

2.4.5 Particle exchange in the path integral picture

- indistinguishable particles: the wave function / thermal density matrix must be symmetric (bosons) or antisymmetric (fermions) under the exchange of particle coordinates (see lecture *Quantum Statistics*). For N particles this leads to $N!$ permutations $\hat{\pi}$

$$Z = \frac{1}{N!} \sum_{\sigma \in S_N} \mathrm{sgn}(\sigma) \int d\mathbf{R} \, \langle R | \, e^{-\beta H} \, | \hat{\pi}_\sigma R \rangle$$

- sum over all elements σ from the N-particle permutation group S_N, where the sign of each permutation is different for bosons and fermions:

$$\mathrm{sgn}(\sigma) = \begin{cases} 1 & \text{bosons,} \\ (-1)^{N_\pi} & \text{fermions} \end{cases}$$

with N_π being the number of pair exchanges for a particular σ (into which a permutation π can be decomposed)

PIMC for bosons and fermions within the primitive approximation

$$Z = \frac{1}{N!} \sum_{\sigma \in S_N} \mathrm{sgn}(\sigma) \int dR_0 \dots dR_{P-1} \left(\prod_{\alpha=0}^{P-2} \rho(R_\alpha, R_{\alpha+1}; \epsilon) \right) \rho(R_{P-1}, \pi_\sigma R_0; \epsilon)$$

Comment: We may also (anti-)symmetrize every time slice
- convenient in practice, “worm algorithm”
Abbildung: permutation cycle, in time and x-y domain

Examples

- *Bose-systems*: e.g. ultracold atoms like ^{4}He
"macroscopic" trajectories with many particles are connected to superfluidity,
Bose-Einstein condensation related to off-diagonal long-range order of the density matrix
$\Rightarrow$ see simulation results of Alexei Filinov
Particle exchange only likely when $\lambda_\beta \sim \bar{r}$
Abbildung

Uniform electron gas:
$\Theta \gg 1$: point-like particles, no exchange effects
$\Theta \sim 1$: $\lambda_\beta \sim \bar{r}$, exchange important, interplay with other effects $\rightarrow$ WDM
$\Theta \ll 1$: system typically fully degenerate, ground state

What we have:

$$Z = \int d\mathbf{X}\, W(\mathbf{X})\,,$$

with "analytical" expression for $W(\mathbf{X})$

What we need: efficient way to evaluate the high-dimensional (3PN) integrals
$\rightarrow$ curse of dimensionality in case of standard quadrature methods

2.4.6 The Metropolis Algorithm

Metropolis, Rosenbluth (x2), Teller (x2), $> 40k$ citations, J. Chem. Phys. 21 (1953)

Problem statement: how to sample a (multi-dimensional) variable $\mathbf{X}$ according to a probability distribution $P(\mathbf{X}) = \frac{W(\mathbf{X})}{Z}$, when the normalization Z is unknown?

Let $P(\mathbf{X} \rightarrow \mathbf{X}')$ be the probability to switch from state $\mathbf{X}$ to $\mathbf{X}'$
detailed balance equation: $P(\mathbf{X} \rightarrow \mathbf{X}') = P(\mathbf{X}' \rightarrow \mathbf{X})$ for all $\mathbf{X}, \mathbf{X}'$

detailed balance ensures stationary $P(\mathbf{X})$, but unnecessarily strict, alternatives do exist (Werner Krauth)

Metropolis-Hastings

$$P(X \rightarrow X') = P(X)T(X \rightarrow X')A(X \rightarrow X')$$

$P(X)$: configuration probability
$T(X \rightarrow X')$: probability to sample X' starting from X
$A(X \rightarrow X')$: probability to accept the proposed move

detailed balance condition:

$$P(X)T(X \rightarrow X')A(X \rightarrow X') = P(X')T(X' \rightarrow X)A(X' \rightarrow X)$$

Metropolis acceptance probability:

$$A(X \to X') = \min\left\{1, \frac{P(X')}{P(X)} \frac{T(X' \to X)}{T(X \to X')}\right\}$$

the unknown normalization Z is the same for $\mathbf{X}$ and $\mathbf{X}'$, $P(\mathbf{X})$, $P(\mathbf{X}')$:

$$A(X \to X') = \min\left\{1, \frac{W(X')}{W(X)} \frac{T(X' \to X)}{T(X \to X')}\right\}$$

Practical contemplation

1. Start with (arbitrary) initial configuration $\mathbf{X}_0$, $|W(\mathbf{X}_0)| > 0$
2. Generate a new configuration $\mathbf{X}'_i$, according to $T(X_i \to X'_i)$
3. Calculate $A(X_i \to X'_i)$. Draw a random number $\alpha \in [0, 1]$. If $\alpha \leq A(x_i \to x'_i)$ the move is accepted and $X_{i+1} = X'_i$, otherwise the move is rejected and $X_{i+1} = X_i$

Repeat steps 2./3. until we have generated a sufficient number of Monte Carlo samples. Given an ergodic set of updates, the algorithm will generate a Markov chain of configurations $\{\mathbf{X}\}$ that are distributed according to $P(\mathbf{X})$

Ergodicity:
- all configurations $\mathbf{X}$ with $W(\mathbf{X}) > 0$ must be reachable in a finite number of steps
- the probability to go from $\mathbf{X}$ to $\mathbf{X}'$ may only depend on $\mathbf{X}$ and $\mathbf{X}'$

Example Markov chain:
Abbildung
Comment:
If an update is rejected, the old config is counted multiple times in the Markov chain. Only counting "accepted" moves is wrong!

Illustration: Metropolis evaluation of a simple integral

$$I = \int_0^\pi x^2 \frac{\sin x}{2}\, dx$$

We can choose

$$P(x) = \begin{cases} \frac{\sin x}{2} & \text{for } x \in [0, \pi] \\ 0 & \text{otherwise.} \end{cases}$$

and

$$W(x) = \begin{cases} \sin x, & \text{for } x \in [0, \pi] \\ 0, & \text{otherwise} \end{cases}$$

Monte Carlo estimator

$$I = \int_0^\pi P(x) \underbrace{x^2}_{\text{estimator } I(x)} dx$$

Metropolis Monte Carlo expectation value

$$I_{MC} = \frac{1}{N_{MC}} \sum_{k=1}^{N_{MC}} I(x_k) = \frac{1}{N_{MC}} \sum_{k=1}^{N_{MC}} x_k^2$$

Simple Monte Carlo update

randomly propose to change x_i by $\pm\delta x$

$$T(x \to x') = \frac{1}{2\Delta x} = T(x' \to x)$$

$$\Rightarrow A(x \to x') = \min\left\{1, \frac{W(x')}{W(x)}\right\} = \min\left\{1, \frac{\sin x'}{\sin x}\right\}$$

- Moves towards larger values of $\sin(x')$ are always accepted
- Moves towards smaller values can be accepted with a finite probability

Task/Exercise

Compute histogram $P(x)$ from this Metropolis MC simulation

Error analysis of Monte-Carlo data

Metropolis Monte-Carlo estimate of integral I only converges for $N_{MC} \to \infty$

$$\lim_{N_{MC} \to \infty} I_{MC} = I$$

What is the statistical error for a finite number of samples I_i?

uncorrelated samples

$$\sigma = \left\{ \frac{1}{N_{MC}} \sum_{i=1}^{N_{MC}} (I_{MC} - I_i)^2 \right\}^{1/2}$$

How much does $I(\mathbf{x})$ fluctuate for different $\mathbf{X}$?

Central limiting theorem (without proof)

- Monte-Carlo expectation value is a random variable that is normally distributed around the exact value of the integral, I
- variance:

$$\sigma_{MC} = \frac{\sigma}{\sqrt{N_{MC}}}$$

- suppose we do M independent MC estimations of some integral with N_{MC} samples each
Abbildung
But: adjacent elements in the Markov chain are correlated
$\Rightarrow$ Number of "effectively independent" MC samples is reduced
Autocorrelation time:

$$\Sigma^{\tau}_{MC^2} = \Sigma^2_{MC} \cdot 2 \underbrace{\tau}_{\text{integrated autocorrelation time}}$$

Filinov/Bonitz chapter in "yellow book" [Be06]
Bottom line: We want a set of efficient MC updates that:
1. propose a "large" random change to $\mathbf{X}$
2. have also a "large" acceptance ratio $\alpha \in [10 \ldots 50\%]$

Example: Volume of a M-dimensional hypersphere

$$\Theta(\mathbf{x}) = \begin{cases} 1, & \text{if } (\mathbf{x} \cdot \mathbf{x}) \leq r^2 \\ 0, & \text{otherwise.} \end{cases}$$

1: Hit-and-miss Monte Carlo, $N_{MC} = 10^6$ samples
Propose random $\mathbf{x}$, with $x_j \in [-r, r]$, Count values of $\Theta(\mathbf{x})$
2: Trapezoidal rule: $R = 25$ intervals

M	time 2. [s]	time 1. [s]	hit-ratio 1.
2	0.000	0.07	0.78
3	$\sim 10^{-4}$	0.09	0.52
4	1.210^{-3}	0.12	0.31
5	0.03	0.14	0.16
6	0.62	0.17	0.08
7	14.9	0.19	$3.7 * 10^{-2}$
8	369	0.22	$1.6 * 10^{-2}$

$$\sigma_{MC} \sim \frac{1}{\sqrt{N_{MC}}}$$

Path sampling scheme

Simple example: The "Deform" Update
1. Select a random piece of trajectory of length M
2. Change the coordinates of the involved beads
Naive: $T(X \to X') = \frac{1}{V^M} = T(X' \to X)$
Problem: Exponentially decaying weights
Importance sampling:
Construct $T(X \to X')$ so that as many parts of $\frac{W(X')}{W(X)}$ are cancelled by the T-ratio in the acceptance probability $A(X \to X')$
- high acceptance ratio
- $\rho_0(r_{i\,\alpha}, r_{i,\alpha+1}; \epsilon)$ is a normal distribution $\Rightarrow$ use for sampling

$$\Rightarrow T(X \to X') = \prod_{\alpha=1}^{M} \rho_0(\mathbf{r}_\alpha, \underbrace{\mathbf{r}_{\alpha+1}}_{\text{coordinates of the M changed beads}}; \epsilon)$$

Problem: the transition between the last new coordinate and the fixed end-point is not taken into account in the sampling
$\Rightarrow \frac{W(x')}{W(x)} \longrightarrow$ low acceptance ratio
Solution: take end-point into account
- draw connection between last existing bead and fixed end-point
- sample new coordinate around the intersection of "present" time slices and this connecting line
- repeat
modified sampling formula:

$$T(X \to X') = \rho_0\left(\mathbf{r}_{start}, \mathbf{r}_{end}; (M+1)\epsilon\right) \times \prod_{\alpha=0}^{M} \rho_0(r_\alpha, r_{\alpha+1}, \epsilon)$$

$$A(X \to X') = \min\left\{1, \frac{W(X')}{W(X)} \frac{T(X' \to X)}{T(X \to X')}\right\} = \min\left\{1\,, e^{-\epsilon \sum\limits_{\alpha=1}^{M} [V(R'_\alpha) - V(R_\alpha)]}\right\}$$

Only the change in the potential energy contributes to the acceptance ratio