Quantum Monte Carlo

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Documents:

- QMC_caffarel.pdf (this talk)
- He_QMC.f90

Generalities on Quantum Monte Carlo

$$\boxed{\text{QMC} \;=\; \text{Solving the Schrödinger equation using stochastic methods}}$$

A great variety of QMC variants developed and applied in various scientific communities. May depend on

- Zero-temperature or finite-temperature
- Statistics: Bose, Fermi, or Boltzmann
- Space: Continuous or discrete

A few examples

- Ground- and excited-states of electrons in molecules: ($T = 0$, Fermi, continuous space)
- Ro-vibrational spectrum of molecules: ($T = 0$, Boltzmann, continuous)
- Superfluidity of He_4 liquids ($T \neq 0$, Bose, continuous space)
- Supraconductivity in the Hubbard model ($T = 0$ and $\neq 0$, Fermi, discrete space)

etc.

Here: Rather **general presentation of QMC at** $T = 0$ with one detailed application to theoretical chemistry (code and results for ground-state energy of the Helium atom)

Is there a common idea to all these QMC variants?

YES!

Two ideas in any QMC method:

I. **Quantum properties written as path integrals** (one way or an other, explicitly or implicity)

II. **Path integrals computed with stochastic (Monte Carlo) methods**

First idea: Quantum properties expressed as path integrals

In QMC we start from the **time-dependent Schrödinger equation**,that is

$$\boxed{i\hbar\frac{\partial|\Psi(t)\rangle}{\partial t} = H|\Psi(t)\rangle}$$

For H **independent on time** the solution is written as

$$\boxed{|\Psi(t)\rangle = e^{-itH}|\Psi(0)\rangle}$$

where $|\Psi(0)\rangle$ is some arbitrary initial state (here, atomic units).

OK! But what the exponential of an operator is?

What we need to know here about operators and exponential of operators

Operators

For a auto-adjoint (hermitic) matrix (or operator) we have the following **spectral decomposition of the operator**

$$\boxed{M = \sum_n \lambda_n |u_n\rangle\langle u_n|}$$

with $|u_n\rangle$ are the orthonormal eigenvectors of M and λ_n eigenvalues

$$M|u_n\rangle = \lambda_n|u_n\rangle$$

The set $\{|u_n\rangle\}$ is a (complete) basis set. Let $|u\rangle$ be an arbitrary vector

$$|u\rangle = \sum_n c_n |u_n\rangle = \sum_n \langle u_n|u\rangle |u_n\rangle = \Big[\sum_n |u_n\rangle\langle u_n\Big]|u\rangle$$

The fact that the sum of projectors over orthogonal eigenspaces is identity is expressed as

$$\boxed{\sum_n |u_n\rangle\langle u_n| = 1}$$

This important expression is usually called the **resolution of the identity**

Exponential of an operator

- Definition

$$\boxed{e^M = \sum_{n=0}^{+\infty} \frac{1}{n!} M^n}$$

To be valid this definition requires that all matrix elements M_{ij} be a *convergent series*.

- **THE** important remark

$$e^{A+B} \neq e^A e^B \quad \text{if } A \text{ and } B \text{ do not commute}$$

Baker-Campbell-Hausdorff (BCH) formula:

$$e^{A+B} = e^A e^B + \frac{1}{2}[A, B] + \frac{1}{12}[(A - B)[A, B] + \ldots$$

The variant of BCH used in QMC

Let us consider a "small" real parameter τ

$$\boxed{e^{-\tau(A+B)} = e^{-\tau A} e^{-\tau B} + O(\tau^2)[A, B] + O(\tau^3) + \ldots}$$

For τ small enough, the corrections due to the commutator become negligible.

- Property 1

$$\boxed{M^k|u_n\rangle = {\lambda_n}^k|u_n\rangle}$$

- Property 2

$$\boxed{e^M|u_n\rangle = e^{\lambda_n}|u_n\rangle}$$

Easy to show from the definition of the exponential of an operator and property 1.

A simple example of non-trivial exponential operator (to be used later on)

$$e^{\frac{\partial}{\partial x}} = ?$$

A simple example of non-trivial exponential operator (to be used later on)

$$e^{\frac{\partial}{\partial x}} = ?$$

$e^{\frac{\partial}{\partial x}}$ = translation operator.

Indeed,
$e^{\frac{\partial}{\partial x}} f(x) = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\partial^n f}{\partial x^n}(x) = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\partial^n f}{\partial x^n}(x)(x+1-x)^n = f(x+1)$

Derivation of the solution of the time-dependent Schrödinger equation

Let us now show that the solution of $i\frac{\partial|\Psi(t)\rangle}{\partial t} = H|\Psi(t)\rangle$ is indeed

$$\boxed{|\Psi(t)\rangle = e^{-itH}|\Psi(0)\rangle}$$

where $\Psi(0)$ is some arbitrary initial vector of the linear space.

Proof. Writing the eigenspectrum of H as

$$H|\phi_n\rangle = E_n|\phi_n\rangle$$

the spectral decomposition of the operator e^{-itH} reads

$$e^{-itH} = \sum_n e^{-itE_n}|\phi_n\rangle\langle\phi_n|$$

Taking the time-derivative of $e^{-itH}|\Psi(0)\rangle$ we get

$$\frac{\partial\left[e^{-itH}|\Psi(0)\rangle\right]}{\partial t} = -i\sum_n E_n e^{-itE_n}|\phi_n\rangle\langle\phi_n|\Psi(0)\rangle$$

$$= -iH\sum_n e^{-itE_n}|\phi_n\rangle\langle\phi_n|\Psi(0)\rangle$$

$$= -iH\left[e^{-itH}|\Psi(0)\rangle\right]$$

Denoting $|\Psi(t)\rangle = e^{-itH}|\Psi(0)\rangle$ we get $i\frac{\partial|\Psi(t)\rangle}{\partial t} = H|\Psi(t)\rangle$
End of the proof.

QMC= Imaginary-time quantum dynamics

QMC is based on the remark that, **as far as we are interested in obtaining the (time-independent) eigensolution of H**, the time t plays no fundamental role, it can be just considered as a parameter.

We have seen that the solution of

$$i\frac{\partial|\Psi(t)\rangle}{\partial t} = H|\Psi(t)\rangle$$

is

$$\boxed{|\Psi(t)\rangle = \sum_n e^{-itE_n} c_n|\phi_n\rangle} \quad c_n = \langle\phi_n|\Psi(0)\rangle$$

Now, while the solution of the same equation by **taking $t \to -it$ (going from real to imaginary-time in QMC)**

$$\boxed{\frac{\partial|\Psi(t)\rangle}{\partial t} = -H|\Psi(t)\rangle}$$

is

$$|\Psi(t)\rangle = e^{-tH}|\Psi(0)\rangle$$

$$\boxed{|\Psi(t)\rangle = \sum_n c_n e^{-tE_n}}$$

In both cases, it is possible to extract E_n and $|\phi_n\rangle$ from the solution.

QMC= Imaginary-time quantum dynamics

Once the solution $|\Psi(t)\rangle$ has been obtained **the low-lying spectrum** is extracted by looking at the **large time behavior** of the solution.

$$|\Psi(t)\rangle = \sum_n c_n |\phi_n\rangle e^{-tE_n}$$

$$|\Psi(t)\rangle = e^{-tE_0}\left[|\phi_0\rangle + \sum_{n\neq 0} e^{-t(E_n - E_0)}\right]$$

$$\boxed{|\Psi(t)\rangle \sim_{t \text{ large}} |\phi_0\rangle + O[e^{-t(E_1-E_0)}]|\phi_1\rangle}$$

QMC= path integral formalism

The quantity to be computed is

$$\Psi(\mathbf{x},t) = \langle \mathbf{x}|e^{-tH}|\Psi(t=0)\rangle$$

It can be written as

$$\Psi(\mathbf{x},t) = \int d\mathbf{x}_0 \langle \mathbf{x}|e^{-tH}|\mathbf{x}_0\rangle \Psi(\mathbf{x}_0,t=0) = \int d\mathbf{x}_0 G(\mathbf{x},\mathbf{x}_0,t)\Psi(\mathbf{x}_0,t=0)$$

where

$$\boxed{G(\mathbf{x},\mathbf{x}_0,t) = \langle \mathbf{x}|e^{-tH}|\mathbf{x}_0\rangle}$$

is the (full) **time-dependent N-body Green's function** (not reduced 2-body Green's function as, for example, in GW).

$G(\mathbf{x}, \mathbf{x}_0, t)$ is the solution of the Schrödinger equation for the initial condition $\Psi(\mathbf{x}_0, t = 0) = \delta(\mathbf{x} - \mathbf{x}_0)$. Its knowledge is sufficient to construct the general solution.

Of course, G **is not known in the general case!!**

To compute it, we shall express it as a **path integral**

Constructing the path integral presentation of G

The time is divided into N small intervals such that $t = N\tau$ and the exponential operator is split

$$e^{-tH} = e^{-\tau H - \tau H ... - \tau H} = e^{-\tau H} e^{-\tau H} ... e^{-\tau H}$$

Now, by inserting the resolution of the identity between each $e^{-\tau H}$ we get the (exact) relation **for any N**

$$G(\mathbf{x}, \mathbf{x}_0, t) = \langle \mathbf{x} | e^{-tH} | \mathbf{x}_0 \rangle$$

$$= \int d\mathbf{x}_1 ... d\mathbf{x}_{N-1} \langle \mathbf{x} | e^{-\tau H} | \mathbf{x}_{N-1} \rangle ... \langle \mathbf{x}_{i+1} | e^{-\tau H} | \mathbf{x}_i \rangle ... \langle \mathbf{x}_1 | e^{-\tau H} | \mathbf{x}_0 \rangle$$

that is

$$\boxed{\text{For any } N \quad G(\mathbf{x}, \mathbf{x}_0, t) = \int d\mathbf{x}_1 ... d\mathbf{x}_{N-1} \prod_{i=0}^{N-1} G(\mathbf{x}_i, \mathbf{x}_{i+1}, \tau) \ \text{ with } \mathbf{x}_N = \mathbf{x}}$$

Consider a short-time approximation of G with an error in τ at least of order 2

$$\boxed{G = G_{\text{approx}} + O(\tau^2)}$$

$$G(\mathbf{x}, \mathbf{x}_0, t) = \int d\mathbf{x}_1 ... d\mathbf{x}_{N-1} \prod_{i=0}^{N-1} \prod_i [G_{approx} + O(\tau^2)]$$

and now we take the $N \to \infty$-limit with t fixed and $\tau = \frac{t}{N}$

$$\boxed{G(\mathbf{x}, \mathbf{x}_0, t) = \lim_{N \to \infty} \int d\mathbf{x}_1 ... d\mathbf{x}_{N-1} \prod_{i=0}^{N-1} G_{approx}(\mathbf{x}_i, \mathbf{x}_{i+1}, \tau)}$$

This is the path-integral expression of the solution of the time-dependent Schrödinger equation.

Integral interpreted as a "path-integral"

Let us call a "path" the following series $(\mathbf{x}_0, \mathbf{x}_1, \ldots, \mathbf{x}_N)$ To integrate over all values of $(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ can be viewed as summing over all paths starting at $\mathbf{x}_0$ of length t

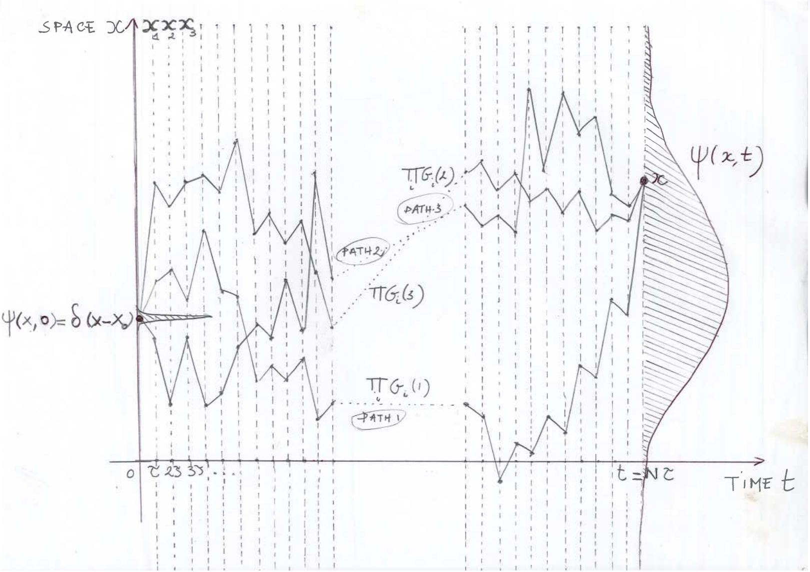


Figure: Pictorial representation of the sum over paths

Searching for a short-time approximation of G

We shall consider a Hamiltonian written under the form

$$H = -\frac{1}{2}\nabla_{\mathbf{x}}^2 + V(\mathbf{x})$$

For example, in theoretical chemistry

$$V = \sum_{i,\alpha} V_{\mathbf{R}_\alpha}(\mathbf{r}_i) + \sum_{i<j} \frac{1}{r_{ij}}$$

Searching for a short-time approximation of G

I. The free case ($V = 0$)

When $V = 0$ the equation to be solved

$$\frac{\partial G_0(\mathbf{x}, \mathbf{x}_0, t)}{\partial t} = -H_0 G_0(\mathbf{x}, \mathbf{x}_0, t) = \frac{1}{2} \nabla_{\mathbf{x}}^2 G_0(\mathbf{x}, \mathbf{x}_0, t)$$

with $G_0(\mathbf{x}, \mathbf{x}_0, 0) = \delta(\mathbf{x} - \mathbf{x}_0)$.

This equation is well-known in physics: heat diffusion, free diffusion equation, etc. Using the Fourier transform of the equation, the solution can be easily obtained (see, appendix D).

$$\boxed{G_0(\mathbf{x}, \mathbf{x}_0, t) = \frac{1}{\sqrt{2\pi t}^d} e^{-\frac{(\mathbf{x} - \mathbf{x}_0)^2}{2t}}}$$

Let us insist that it is a product of one-dimensional gaussian

$$G_0 = \prod_{i=1}^{d} \frac{1}{\sqrt{2\pi t}} e^{-\frac{(x^i - {x_0}^i)^2}{2t}}$$

where $\mathbf{x} = (x^1, \ldots, x^d)$

Searching for a short-time approximation of G

II. The general case, $V \neq 0$

Based on the fact that

$$e^{-\tau H} = e^{-\tau(H_0+V)} = e^{-\tau H_0} e^{-\tau V} + O[\tau^2]$$

$$G(\mathbf{x},\mathbf{x}_0,\tau) = \langle \mathbf{x}|e^{-\tau H}|\mathbf{x}_0\rangle \sim \langle \mathbf{x}|e^{-\tau H_0} e^{-\tau V})|\mathbf{x}_0\rangle$$

$$= \int d\mathbf{x}' \langle \mathbf{x}|e^{-\tau H_0}|\mathbf{x}'\rangle\langle \mathbf{x}'|e^{-\tau V}|\mathbf{x}_0\rangle$$

We have

$$\langle \mathbf{x}'|e^{-\tau V}|\mathbf{x}_0\rangle = e^{-\tau V(\mathbf{x}')}\delta(\mathbf{x}' - \mathbf{x}_0)$$

So

$$\boxed{G_{approx}(\mathbf{x},\mathbf{x}_0,\tau) = G_0(\mathbf{x},\mathbf{x}_0,\tau)e^{-\tau V(\mathbf{x})}}$$

Let us summarize

The **exact solution** of the (imaginary) time-dependent Schrödinger equation can be written as

$$\Psi(\mathbf{x},t) = \int d\mathbf{x}_0 \langle \mathbf{x}| e^{-tH} |\mathbf{x}_0\rangle \Psi(\mathbf{x}_0, t=0) = \int d\mathbf{x}_0 G(\mathbf{x},\mathbf{x}_0,t)\Psi(\mathbf{x}_0,t=0)$$

with

$$G(\mathbf{x},\mathbf{x}_0,t) = \lim_{N\to\infty} \ _{\tau=t/N} \int d\mathbf{x}_1 \ldots d\mathbf{x}_{N-1} \prod_{i=0}^{N-1} G_0(\mathbf{x}_i,\mathbf{x}_{i+1},\tau) e^{-\tau \sum_{i=1}^{N} V(\mathbf{x}_i)}$$

with

$$G_0(\mathbf{x}_i,\mathbf{x}_{i+1},\tau) = \frac{1}{\sqrt{2\pi\tau}^d} e^{-\frac{(\mathbf{x}_i-\mathbf{x}_{i+1})^2}{2\tau}}$$

In particular at large time,
$G(\mathbf{x},\mathbf{x}_0,t) = \phi_0(\mathbf{x})\phi_0(\mathbf{x}_0)e^{-tE_0} + O[e^{-t(E_1-E_0)}|\phi_1\rangle]$, so we can write and

$$\boxed{\phi_0(\mathbf{x}) = \lim_{t\to\infty} \lim_{N\to\infty \ \tau=t/N} \int d\mathbf{x}_1 \ldots d\mathbf{x}_{N-1} \prod_{i=0}^{N-1} G_0(\mathbf{x}_i,\mathbf{x}_{i+1},\tau) e^{-\tau \sum_{i=1}^{N} V(\mathbf{x}_i)}}$$

A formidable result: The solution of the general

Schrödinger equation is written as a multi-dimensional integral of a known function!!! ⇒ Computable!!

Formal writing of the Feynman path-integral

$$\prod G_0 = \prod \frac{1}{\sqrt{2\pi\tau}^d} e^{-\frac{1}{2}\sum_{i=1}^d \frac{(\mathbf{x}^i - \mathbf{x}_0^i)^2}{\tau}} = \prod \frac{1}{\sqrt{2\pi\tau}^d} e^{-\frac{\tau}{2}\sum_{i=1}^d \left(\frac{(\mathbf{x}^i - \mathbf{x}_0^i)}{\tau}\right)^2}$$

So

$$\boxed{\prod G_0 = e^{-\int_0^t ds T[\mathbf{x}(s)]}}$$

where T is the classical kinetic energy functional of the "path" (not classical trajectory!)

$$T = \frac{1}{2}\frac{\partial \mathbf{x}(t)}{\partial t}^2$$

and, similarly

$$\boxed{\prod e^{-V} = e^{-\int_0^t ds V[\mathbf{x}(s)]}}$$

So, finally, we have the formal expression for the ground-state

$$\boxed{\phi_0(\mathbf{x}) = \sum_{\text{paths}} e^{-\int_0^t ds T[\mathbf{x}(s)]} e^{-\int_0^t ds V[\mathbf{x}(s)]}}$$

How to compute the path integral?

The use of Brownian trajectories

The quantity

$$\prod_{i=0}^{N-1} G_0(\mathbf{x}_i, x_{i+1}, \tau) = e^{-\int_0^t ds T[\mathbf{x}(s)]}$$

is the probabilily density associated with **brownian trajectories**

What is a Brownian motion? A one-dimensional brownion motion is a stochastic process (series of random variables dependent on a time t, see appendix C) characterized by the following gaussian probability density distribution:

$$p(x \to x', \tau) = \frac{1}{\sqrt{2\pi\tau}} e^{-\frac{1}{2}\frac{(x-x')^2}{\tau}}$$

A realization (path) of the brownian motion can be written as

$$\text{path} = (x_0, x_1, ..., x_i, x_{i+1}, ..)$$

The brownian process is a so-called **Markov process** (see, appendix C) in the sense that going from x_i at time t_i to x_{i+1} at time t_{i+1} does not depend on what the values of x taken in times preceding t_i (that is, $..., x_{i-2}, x_{i-1}$)

Mathematically, it means that **the probability of the path**

$P(x_0, t = 0; x_1, t_1 = \tau, ..., x_N, t_N = N\tau)$ factorizes as

$$\boxed{\text{Proba of path } = p(x_0 \to x_1, \tau)p(x_1 \to x_2, \tau)...p(x_{N-1} \to x_N, \tau)}$$

Here,

$$\prod_{i=0}^{N-1} G_0(\mathbf{x}_i, x_{i+1}, \tau)$$

is the probability density of a Brownian in d-dimension (each coordinate being independent).

How to generate Brownian trajectories?

Very easy! The probability density to simulate

$$p(x_0^i \to x^i, \tau) = \frac{1}{\sqrt{2\pi\tau}} e^{-\frac{1}{2}\frac{(x^i - x_0^i)^2}{\tau}}$$

The distribution of the normal law (gaussian with zero mean and variance=1) is

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

Here, the normal law is obeyed by

$$g = \frac{x^i - x_0^i}{\sqrt{\tau}}$$

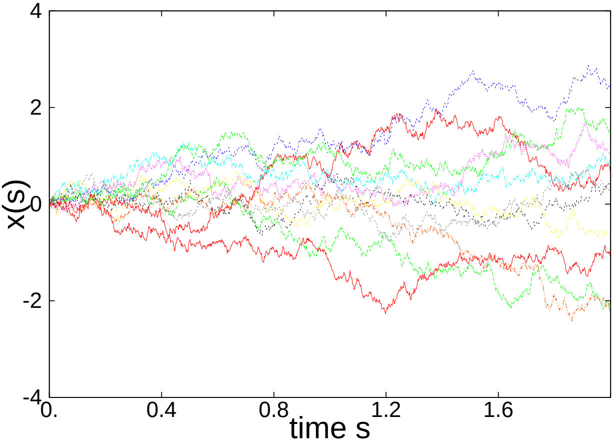
Now, we rewrite this equality as

$$\boxed{x^i = x_0^i + \sqrt{\tau}\mathrm{g}}$$

where g is a random number drawn with the normal distribution (easy to simulate, for example using the Box-Muller algorithm, see appendix B).

This is the **simplest example of a stochastic differential equation** (overdamped Langevin-type stochastic equation)

Some brownian "walkers" in 1D starting at $x = 0$



Monte Carlo calculation of the path integrals using brownian paths

$$\boxed{\phi_0(\mathbf{x}) = \sum_{\text{brownian paths arriving at } \mathbf{x}} e^{-\int_0^{+\infty} ds V[\mathbf{X}(s)]}}$$

but calculating the integral by drawing brownian trajectories is just hopeless!!

The quantity $e^{-\int_0^{+\infty} ds V[\mathbf{X}(s)]}$ varies too wildly as a function of the paths

Why?

Paths generated **are blind with respect to the coulombic potential**, they visit the configuration space uniformly.

$\Rightarrow$ we need to **"guide" the brownian trajectories** in regions of importance for the exact wavefunction $\Phi_0(\mathbf{x})$.

This is beautifully realized in QMC using a trial wavefunction, Ψ_T.

Introducing the trial wavefunction into the imaginary-dynamics

The time-dependent Schrödinger equation in imaginary-time

$$\boxed{\frac{\partial \Psi(\mathbf{x}, t)}{\partial t} = -H\Psi(\mathbf{x}, t) = \frac{1}{2}\nabla^2\Psi(\mathbf{x}, t) - V(\mathbf{x})\Psi(\mathbf{x}, t)}$$

$\Psi_T(\mathbf{x})$ = approximate trial wavefunction
Let us introduce a new density

$$\boxed{f(\mathbf{x}, t) \equiv \Psi_T(\mathbf{x})\Psi(\mathbf{x}, t)} \tag{1}$$

Multiplying each side of the Schrödinger equation by Ψ_T, we get

$$\frac{\partial f(\mathbf{x}, t)}{\partial t} = -\Psi_T(\mathbf{x})H\frac{1}{\Psi_T(\mathbf{x})}f(\mathbf{x}, t)$$

After simple algebra, see appendix F, we get

$$-\Psi_T(\mathbf{x})H\frac{1}{\Psi_T(\mathbf{x})} = \frac{1}{2}\nabla^2 - \nabla[\mathbf{b}(\mathbf{x}).] - E_L(\mathbf{x})$$

where the drift vector is given by

$$\boxed{\mathbf{b}(\mathbf{x}) = \frac{\nabla\Psi_T}{\Psi_T}}$$

and the local energy

$$\boxed{E_L(\mathbf{x}) = \frac{H\Psi_T}{\Psi_T}}$$

New equation of evolution

$$\boxed{\frac{\partial f(\mathbf{x},t)}{\partial t} = \frac{1}{2}\nabla^2 f(\mathbf{x},t) - \nabla[\mathbf{b}(\mathbf{x})f(\mathbf{x},t)] - E_L(\mathbf{x})f(\mathbf{x},t)}$$

Regarding the path integral representation of the solution, we are **exactly in the same situation as before** except that

- the "bare" potential $V(\mathbf{x})$ is replaced by the "screened" potential $E_L(\mathbf{x}) = \frac{H\psi_T}{\psi_T}$

- the free diffusion equation

$$\frac{\partial \Psi}{\partial t} = \frac{1}{2}\nabla^2\Psi$$

is replaced by a new diffusion equation including a drift vector

$$\frac{\partial f}{\partial t} = \frac{1}{2}\nabla^2 f - \nabla[\mathbf{b}f]$$

The short-time approximation of the bare equation

$$\boxed{G = \langle \mathbf{x} | e^{\tau \frac{1}{2}\nabla^2 \cdot} | \mathbf{x}_0 \rangle e^{-\tau V(\mathbf{x})} = \frac{1}{\sqrt{2\pi\tau}^d} e^{-\frac{(\mathbf{x}-\mathbf{x}_0)^2}{2\tau}} e^{-\tau V(\mathbf{x})}}$$

becomes (see derivation in appendix G)

$$\boxed{G = \langle \mathbf{x} | e^{\tau \frac{1}{2}\nabla^2 . - \tau \nabla [\mathbf{b}.]} | \mathbf{x}_0 \rangle e^{-\tau E_L(\mathbf{x})} = \frac{1}{\sqrt{2\pi\tau}^d} e^{-\frac{(\mathbf{x}-\mathbf{x}_0-\mathbf{b}(\mathbf{x}_0)\tau)^2}{2\tau}} e^{-\tau E_L(\mathbf{x})}}$$

As seen, **the effect of the drift term is to just to translate the new point of a quantity $\mathbf{b}(\mathbf{x}_0)\tau$.**

$e^{\frac{\partial}{\partial x}}$ = translation operator ; $e^{-\tau \mathbf{b}(\mathbf{x}_0)\nabla} f(\mathbf{x}) = f(\mathbf{x} - \mathbf{b}(\mathbf{x}_0)\tau)$

So the expression

$$\boxed{\phi_0(\mathbf{x}) \sim \sum_{\text{brownian paths arriving at } \mathbf{x}} e^{-\int_0^{+\infty} ds V[\mathbf{x}(s)]}}$$

is replaced now by

$$\boxed{\phi_0(\mathbf{x})\Psi_T(\mathbf{x}) \sim \sum_{\textbf{drifted}\text{brownian paths arriving at } \mathbf{x}} e^{-\int_0^{+\infty} ds \mathbf{E_L}[\mathbf{x}(s)]}}$$

See, the detailed derivation in appendix H.

Two wonderful effects!

1. The **wild potential** $V(\mathbf{x})$ is replaced by a **smoothly varying potential** $E_L(\mathbf{x})$

Zero-variance property: the variation of $E_L(\mathbf{x})$ and, thus, **the statistical fluctuations vanishes when** $\Psi_T = \Phi_0$

2. The drifted brownian motion becomes

$$\mathbf{x}_{i+1} = \mathbf{x}_i + \mathbf{b}(\mathbf{x}_i)\tau + \sqrt{\tau} gauss$$

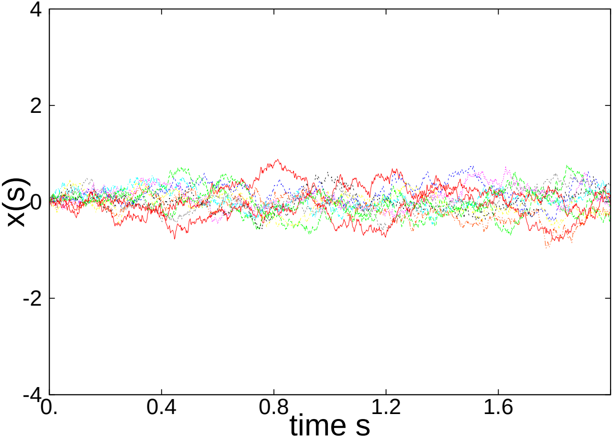
The effect of the drift **b**

$$\mathbf{b} = \frac{\nabla \ \Psi_T}{\Psi_T}$$

is to **push the configurations** from the region where Ψ_T is small toward the region where Ψ_T is large

Now...Using gaussian trial wavefuction

$$\Psi_T(x) = e^{-\frac{x^2}{2}} \quad \mathbf{b} = \frac{\nabla \; \Psi_T}{\Psi_T} = -x$$



Computing the energy

$$\phi_0(\mathbf{x})\Psi_T(\mathbf{x}) \sim \sum_{\text{paths} \ \mathbf{x}(\mathrm{t})=\mathbf{x}} e^{-\int_0^{+\infty} dsE_L[\mathbf{x}(s)]}$$

H being an auto-adjoint operator we can write

$$E_0 = \frac{\int d\mathbf{x} H\Phi_0(\mathbf{x})\Psi_T(\mathbf{x})}{\int d\mathbf{x}\phi_0(\mathbf{x})\Psi_T(\mathbf{x})} = \frac{\int d\mathbf{x}\phi_0(\mathbf{x})H\Psi_T(\mathbf{x})}{\int d\mathbf{x}\phi_0(\mathbf{x})\Psi_T(\mathbf{x})}$$

and then

$$E_0 = \frac{\int d\mathbf{x} E_L(\mathbf{x})\left[\Phi_0(\mathbf{x})\Psi_T(\mathbf{x})\right]}{\int d\mathbf{x}\left[\Phi_0(\mathbf{x})\Psi_T(\mathbf{x})\right]}$$

$$E_0 = \lim_{t\to\infty} \frac{\sum_{\text{paths} \ \mathbf{x}(\mathrm{t})=\text{any} \ \mathbf{x}} E_L(\mathbf{x}(t))\left[e^{-\int_0^t dsE_L[\mathbf{x}(s)]}\right]}{\sum_{\text{paths} \ \mathbf{x}(\mathrm{t})=\text{any} \ \mathbf{x}}\left[e^{-\int_0^t dsE_L[\mathbf{x}(s)]}\right]}$$

Helium atom

$$\mathbf{x} = (\mathbf{r}_1, \mathbf{r}_2)$$

$$\Psi_T = (1 + \alpha r_{12}) e^{-\gamma(r1+r2)}$$

Drift and local energy:

$$u(r_{12}) = \frac{\alpha}{1 + \alpha r_{12}}$$

$$\mathbf{b}_1 = \frac{\nabla_1 \Psi_T}{\Psi_T} = -\gamma \frac{\mathbf{r}_1}{r_1} + u(r_{12}) \frac{\mathbf{r}_{12}}{r_{12}}$$

$$\mathbf{b}_2 = \frac{\nabla_2 \Psi_T}{\Psi_T} = -\gamma \frac{\mathbf{r}_2}{r_2} + u(r_{12}) \frac{\mathbf{r}_{21}}{r_{12}}$$

$$E_L = (\gamma - 2)(\frac{1}{r_1} + \frac{1}{r_2}) + \frac{1}{r_{12}} - \gamma^2 + u(r_{12})\big[-\frac{2}{r_{12}} + \gamma \frac{\mathbf{r}_{12}}{r_{12}} (\frac{\mathbf{r}_1}{r_1} - \frac{\mathbf{r}_2}{r_2})\big]$$

Hartree-Fock energy: -2.8616..

Exact non-relativistic energy (CBS) -2.90372...

Full code (working as it is!!) for the Helium atom in 3 pages!

```
program qmc
parameter(m_max=200)
real x0(3,2),xold(3,2),xnew(3,2),drift(3,2)
real h(m_max),s(m_max)
double precision random

print*,'N?'
read*,n_paths
tau=0.0375
alpha=0.35
gam=2.
```

```
do i=1,2   ! electrons 1 and 2
 do l=1,3  ! x y z
  call random_number(random)
  x0(l,i)=random-0.5
 enddo
enddo

h=0.
s=0.
do i_path=1,n_paths

 do i=1,2
  do l=1,3
   xold(l,i)=x0(l,i)
  enddo
 enddo

 prod=1.  ! initialization of prod =\prod_{i=1}^{m_max} exp(-tau E_loc(i))
```

```
 do j=1,m_max  ! stochastic path t=0 to t=m_max*tau

  call compute_drift(xold,b,gam,alpha)
  do i=1,2
   do l=1,3
    xnew(l,i)=xold(l,i)+drift(l,i)*tau+sqrt(tau)*gauss() ! stochastic diff. eq.
   enddo
  enddo
  eloc=compute_elocal(xnew,gam,alpha)  ! local energy
  prod=prod*exp(-tau*eloc)
  h(j)=h(j)+prod*eloc
  s(j)=s(j)+prod
  xold=xnew
 enddo  !  end of the stochastic path

enddo  !  loop over paths

do j=1,m_max
 write(*,*)'time', j*tau,'Energy=',h(j)/s(j)
 write(33,*)j*tau,h(j)/s(j)
enddo
end
```

```
subroutine compute_drift(x,b,gam,alpha)
real x(3,2),b(3,2),r(2)
do i=1,2
 r(i)=sqrt(x(1,i)**2+x(2,i)**2+x(3,i)**2)
 do l=1,3
  b(l,i)=-gam*x(l,i)/r(i)
 enddo
enddo
r12=sqrt((x(1,1)-x(1,2))**2+(x(2,1)-x(2,2))**2+(x(3,1)-x(3,2))**2)
u=alpha/(1.+alpha*r12)
do l=1,3
 b(l,1)=b(l,1)+u*(x(l,1)-x(l,2))/r12
 b(l,2)=b(l,2)+u*(x(l,2)-x(l,1))/r12
enddo
end
```

```
function compute_elocal(x,gam,alpha)
real x(3,2),r(2)
r(1)=sqrt(x(1,1)**2+x(2,1)**2+x(3,1)**2)
r(2)=sqrt(x(1,2)**2+x(2,2)**2+x(3,2)**2)
r12=sqrt((x(1,1)-x(1,2) )**2+ (x(2,1)-x(2,2) )**2 + (x(3,1)-x(3,2) )**2)
elocal= (gam-2.)*(1./r(1) + 1./r(2)) + 1./r12 -gam**2
u=alpha/(1.+alpha*r12)
prod=0.
do l=1,3
 prod=prod+(x(l,1)-x(l,2))/r12*(x(l,1)/r(1)-x(l,2)/r(2))
enddo
elocal=elocal-2.*u/r12 + gam*u*prod
end
```

```
!Box Muller gaussian generator
function gauss()
double precision random
twopi=2.*acos(-1.)
call random_number(random)
u=log(random)
call random_number(random)
gauss=sqrt(-2.*u)*cos(twopi*random)
end
```

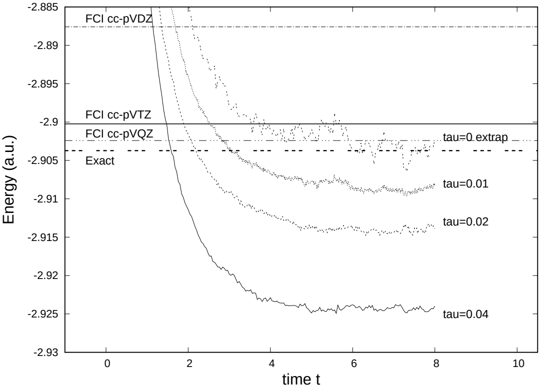


Figure: Convergence of the ground-state energy of He as a function of t. $\tau = 0.04, 0.02$, and $0.001, \gamma = 2, \alpha = 0.35, N_{\mathrm{paths}} = 10^6$

Pauli principle

We have shown how to solve with QMC the Schrödinger equation

$$H\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$$

using **electrons spatial positions only**.

What about the spin?

In the **usual spin-space formalism**

$$\Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; ..., \mathbf{r}_N \sigma_N) \;\; \sigma = \alpha \text{ or } \beta$$

$\Psi \to -\Psi$ when exchanging any pair of electrons $(\mathbf{r}_i, \sigma_i) \leftrightarrow (\mathbf{r}_j, \sigma_j)$

- Ground-state of He atom

$$\Psi \sim \begin{vmatrix} 1s(\mathbf{r}_1)\alpha & 1s(\mathbf{r}_2)\alpha \\ 1s(\mathbf{r}_1)\beta & 1s(\mathbf{r}_2)\beta \end{vmatrix}$$

- Ground-state of Li atom

$$\Psi \sim \begin{vmatrix} 1s(\mathbf{r}_1)\alpha & 1s(\mathbf{r}_2)\alpha & 2s(\mathbf{r}_3)\alpha \\ 1s(\mathbf{r}_1)\beta & 1s(\mathbf{r}_2)\beta & 2s(\mathbf{r}_3)\beta \\ 2s(\mathbf{r}_1)\alpha & 2s(\mathbf{r}_2)\alpha & 2s(\mathbf{r}_3)\alpha \end{vmatrix}$$

In a pure-space formalism

$$\Psi(\mathbf{r}_1^{\alpha}, .., \mathbf{r}_{N_\alpha}^{\alpha}; \mathbf{r}_1^{\beta}, .., \mathbf{r}_{N_\beta}^{\beta}) \quad \text{with} \quad N = N_\alpha + N_\beta$$

$\boxed{\Psi \to -\Psi \text{ when exchanging any pair of } \textbf{spin-like electrons } \mathbf{r}_i^{\sigma} \leftrightarrow \mathbf{r}_j^{\sigma}}$

- He atom

$$\Psi \sim 1s(\mathbf{r}_1)1s(\mathbf{r}_2)$$

- Lithium atom (electrons 1 and 2 chosen to be α, electron 3 to be β)

$$\Psi \sim \begin{vmatrix} 1s(\mathbf{r}_1) & 1s(\mathbf{r}_2) \\ 2s(\mathbf{r}_1) & 2s(\mathbf{r}_2) \end{vmatrix} 1s(\mathbf{r}_3)$$

But

$$\Psi \sim 1s(\mathbf{r}_1)1s(\mathbf{r}_2)1s(\mathbf{r}_3)$$

Three electrons in the 1s for the Lithium atom!!! Not allowed !! But such a state exists, it is a **bosonic state**!!

In theory, everything works as it is!!

Let us come back to the exact solution

$$\Psi_T(\mathbf{x})\phi_0(\mathbf{x}) \sim_{t\to\infty} \sum_{\text{paths } \mathbf{x}(\text{t})=\text{x}} e^{-\int_0^t ds E_L[\mathbf{x}(s)]}$$

At finite t and not imposing $\mathbf{x}$

$$\langle \Psi_T | e^{-tH} | \mathbf{x}_0 \rangle = \sum_{\text{paths } \mathbf{x}(\text{t})=\text{any } \mathbf{x}} e^{-\int_0^t ds E_L[\mathbf{x}(s)]}$$

If Ψ_T is properly antisymmetrized:

$$\langle \Psi_T | e^{-tH} | \mathbf{x}_0 \rangle = \sum_n e^{-E_n t} \langle \phi_n | \Psi_T \rangle \phi_n(\mathbf{x}_0)$$

with ϕ_n are **either bosonic or fermionic** However,

$$\boxed{\langle \phi_n^{\text{boson}} | \Psi_T \rangle = 0}$$

so

$$\sum_n e^{-E_n^{\text{fermion}} t} \langle \phi_n^{\text{fermion}} | \Psi_T \rangle \phi_n^{\text{fermion}}(\mathbf{x}_0)$$

and at large time **the fermionic ground-state is obtained**

What is the problem?

Ψ_T antisymmetric can vanish !!

For example, when two spin-like electrons are at the same position.

At these locations **the drift vector**

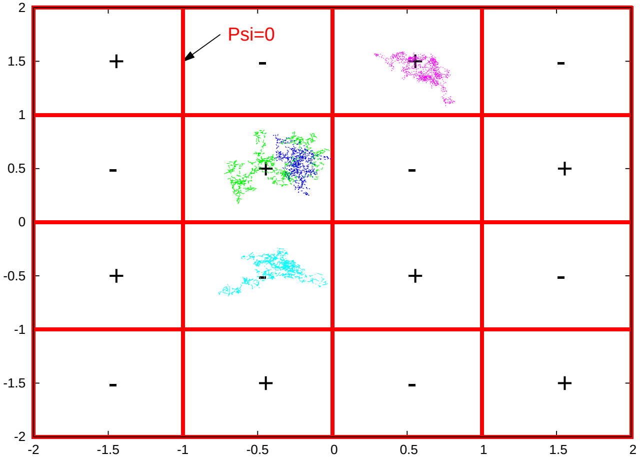
$$b = \frac{\nabla\ \Psi_T}{\Psi_T}$$

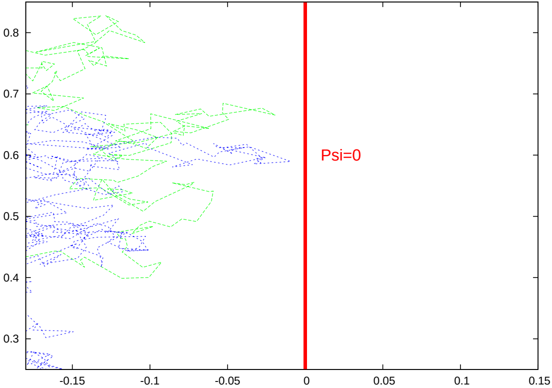
diverges.

The zeroes of Ψ_T are called the **nodes (nodal hypersurfaces in dimension $3d-1$) of the trial wavefunction.**

The nodes play the role of **repulsive barriers for the walkers**

⇒ **Walkers are trapped for ever in domains delimited by the nodes!**




0.8
0.7
0.6
0.5
0.4
0.3
-0.15
-0.1
-0.05
0
0.05
0.1
0.15
Psi=0

What problem do we solve exactly?

Walkers remain for ever in domains of **constant sign for Ψ_T** ("nodal pockets")

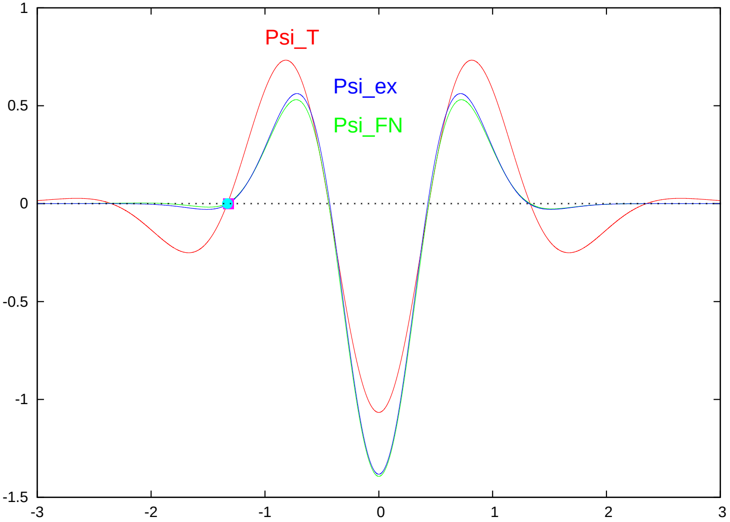
$$\phi_0(\mathbf{x})\Psi_T(\mathbf{x}) = \sum_{\text{paths}} e^{-\int dsE_L} > 0$$

The Schrödinger equation is solved with the additional constraint that **the solution has the same sign** as Ψ_T [**Fixed-node (FN) approximation**]

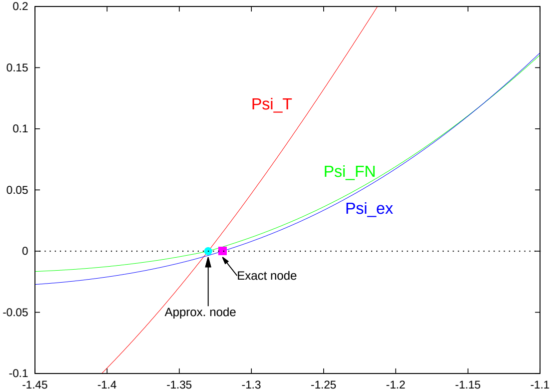
$$\boxed{H\Psi_{FN} = E_{FN}\Psi_{FN}}$$

Note that there is a variational property

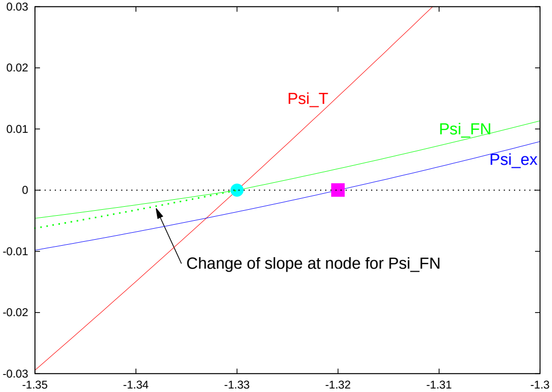
$$E_{FN} \geq E_0$$


Psi_T
Psi_ex
Psi_FN
1
0.5
0
-0.5
-1
-1.5
-3
-2
-1
0
1
2
3

Zoom


0.2
0.15
0.1
0.05
0
-0.05
-0.1
-1.45
-1.4
-1.35
-1.3
-1.25
-1.2
-1.15
-1.1
Psi_T
Psi_FN
Psi_ex
Exact node
Approx. node

Zoom of the zoom



Exact QMC simulations: The sign problem

If we want to avoid this problem, we must take a **non-vanishing trial wavefunction** (that is, a bosonic-type wavefunction) and **add an antisymmetric weight into the averages** to project out on the fermionic ground-state.

For example, bosinization of Ψ_T

$$\Psi_T^{boson} = \sqrt{\Psi_T^2 + \epsilon}$$

and weight

$$w = \frac{\Psi_T}{\Psi_T^{boson}} = w_+ - w_-$$

$$\langle \Psi_T | e^{-tH} | \mathbf{x}_0 \rangle = \sum_{\text{paths}} e^{-\int_0^t ds E_L[\mathbf{x}(s)]} w(t)$$

which gives

$$\boxed{\langle \Psi_T | e^{-tH} | \mathbf{x}_0 \rangle = \sum_{\text{paths}} \left[e^{-\int_0^t ds E_L[\mathbf{x}(s)]} w_+(t) - e^{-\int_0^t ds E_L[\mathbf{x}(s)]} w_-(t) \right]}$$

It can be easily shown that **the fluctuations of the sign of the average make the simulation wildely unstable** To solve this problem is considered as **one of the most important problem of computational physics**

Some references on Variational Monte Carlo (VMC) and Diffusion Monte Carlo (DMC)

- **For continous systems**

1) W.M.C Foulkes, L. Mitas, R.J. Needs, G. Rajagopal *Quantum Monte Carlo simulations of solids* Rev. Mod. Phys., vol=73, 33-83 (2001)(2001)

2) J. Kolorenc and L. Mitas, Rep. Prog. Phys. vol.74, 026502 (2011)

3) C.J. Umrigar *Observations on variational and projector Monte Carlo methods* J. Chem. Phys., vol=143, 164105 (2015)

4) J. Toulouse, R. Assaraf, and C. J. Umrigar, *Introduction to the variational and diffusion Monte Carlo methods*, Advances in Quantum Chemistry, Elsevier,series = Electron Correlation in Molecules – ab initio Beyond Gaussian Quantum Chemistry, vol. 73,285 (2016).

- **For finite matrices**

1) M. Caffarel and R. Assaraf, *A pedagogical introduction to quantum Monte Carlo* Lecture Notes in Chemistry, editor=M. Defranceschi and C. Le Bris, Springer, 45, (2000)

We will stop the course here. What follows describes more specialized aspects.

The Variational Monte Carlo (VMC) method

In VMC, the probability density associated with Ψ_T is sampled

$$\pi(\mathbf{x}) = \frac{\Psi_T^2(\mathbf{x})}{\int d\mathbf{x}\Psi_T^2(\mathbf{x})^2}.$$

The properties are computed as probabilistic averages over sampled configurations.
In the case of the energy, the variational energy E_v is obtained as

$$E_v = \frac{\langle\Psi_T|H|\Psi_T\rangle}{\langle\Psi_T|\Psi_T\rangle} = \frac{\int d\mathbf{x}|\Psi_T|^2\frac{H\Psi_T}{\Psi_T}}{\int d\mathbf{x}|\Psi_T|^2}$$

that is

$$\boxed{E_v = \int d\mathbf{x}\pi(\mathbf{x})E_L(\mathbf{x})}$$

$$E_{var} = \langle E_L \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{N} E_L(\mathbf{x}_i)$$

Other properties can be computed in a similar way

$$\frac{\langle \Psi_T | O | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} = \int d\mathbf{x} O(\mathbf{x}) \pi(\mathbf{x}) = \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{K} O(\mathbf{x}_i)$$

How to sample Ψ^2?

- Use of the drifted brownian motion.

$$\boxed{\frac{\partial f(\mathbf{x},t)}{\partial t} = \frac{1}{2}\nabla^2 f(\mathbf{x},t) - \nabla[\mathbf{b}(\mathbf{x})f(\mathbf{x},t)]}$$

The stationary distribution is given by the condition

$$\frac{\partial f(\mathbf{x},t)}{\partial t} = 0$$

which gives

$$f(\mathbf{x}) = \frac{\Psi_T^2}{\int d\mathbf{x}\Psi_T^2}$$

Proof.

$$\frac{1}{2}\nabla^2 f - \nabla[\mathbf{b}f] = \frac{1}{2}\nabla^2\Psi_T^2 - \nabla\frac{\nabla\Psi_T}{\Psi_T}\Psi_T^2 = \frac{1}{2}\nabla^2\Psi_T^2 - \frac{1}{2}\nabla\nabla\Psi_T^2 = 0$$

The averages can be computed over the set of configurations generated by the drifted brownian motion.

Nice but practical problem is the residual **short-time error** due to the finite time-step τ.

•Use of the Metropolis algorithm

Very important algorithm.

It belong to **the Top 10 list of the most employed numerical algorith used in science and technology**

The Metropolis algorithm

The aim is to compute

$$\boxed{\mathrm{I} = \int_{\mathcal{E}} d\mathbf{x}\pi(\mathbf{x})F(\mathbf{x})}$$

where $\mathbf{x} \in \mathcal{E}=$ configuration space (continuous or discrete).
$\pi(\mathbf{x})$ probability density, that is

$$\pi(\mathbf{x}) \geq 0 \quad \text{and} \quad \int_{\mathcal{E}} d\mathbf{x}\; \pi(\mathbf{x}) = 1$$

The Metropolis algorithm generates step by step configurations $\mathbf{x}^i$ in configuration space distributed according to $\pi(\mathbf{x})$.
We then have

$$\mathrm{I} = \lim_{P\to\infty} \frac{1}{P} \sum_{i=1}^{P} F(\mathbf{x}^i)$$

In practice, a finite number of configurations are generated and we have

$$\mathrm{I} = \frac{1}{\mathrm{P}}\sum_{\mathrm{i}=1}^{\mathrm{P}} \mathrm{F}(\mathrm{x}^{\mathrm{i}}) + \frac{\mathrm{c}}{\sqrt{\mathrm{P}}} \quad \text{for P large enough}$$

The fundamental quantity of the algorithm is the **trial transition probability density** denoted here as $P(\mathbf{x} \rightarrow \mathbf{y})$.

The algorithm is as follows.

METROPOLIS ALGORITHM

At each Monte Carlo step a new state $\mathbf{x}_{i+1}$ is generated from the current state $\mathbf{x}_i$ by a two-step procedure:

1) Draw a “trial” state denoted as $\mathbf{x}^T$ using the trial transition probability density $P(\mathbf{x} \to \mathbf{y})$

2) Accept the trial state as the new state ($\mathbf{x}_{i+1} = \mathbf{x}^T$) or reject it ($\mathbf{x}_{i+1} = \mathbf{x}_i$) with probability $q(\mathbf{x}_i, \mathbf{x}_T)$ $(0 \leq q \leq 1)$ given by

$$q = Min\left[1, \frac{\pi(\mathbf{x}^T)P(\mathbf{x}^T \to \mathbf{x}_i)}{\pi(\mathbf{x}_i)P(\mathbf{x}_i \to \mathbf{x}^T)}\right] \tag{2}$$

- $P(\mathbf{x} \to \mathbf{y})$ **must be easy to sample.** In practice, we (almost) always use a product of one-dimensional uniform or gaussian probability densisities. A universal choice inspired by the drifted brownian motion defined above is

$$P(\mathbf{x} \to \mathbf{y}) = \frac{1}{\sqrt{2\pi\tau}^{d}} e^{-\frac{(\mathbf{x}-\mathbf{x}_0-\mathbf{b}(\mathbf{x}_0)\tau)^2}{2\tau}}$$

where the drift is

$$\mathbf{b}(\mathbf{x}) = \frac{1}{2}\frac{\nabla\pi}{\pi}$$

- $P(\mathbf{x} \to \mathbf{y})$ **must be ergodic** ("go everywhere")

- The Metropolis algorithm converges to π **independently** on the choice of the trial transition probability and/or the initial conditions $\mathbf{x}_0$.

Such quantities only determines the rate of convergence of the Markov chain towards π.

For a derivation of the Metropolis algorithm in the discrete case, see appendix E

The trial wavefunction

In QMC a great freedom in choosing the functional form of the trial wavefunction

The standard choice: The multi-determinant Slater-Jastrow wavefunction.

$$\Psi_T = e^{J(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \sum_{k=1}^{N_{det}} c_k Det_k(\{\Phi_i^\alpha\}) Det_k(\{\Phi_i^\beta\}), \tag{3}$$

where $\{\Phi_i^\sigma\}(\sigma = \alpha, \beta)$ is a set of molecular orbitals and e^J is the Jastrow factor.

The role of the Jastrow factor is to impose the exact behavior of the wavefunction in the $[r_{ij} \to 0]$-limit (electron-electron cusp condition) and, also, to incorporate some two-body (electron-electron and electron-nucleus) and three-body (electron-electron-nucleus) correlations (to describe the best as possible the shape of the Coulomb hole[**?**]). Many different forms for the Jastrow factor have been introduced. Typically,

$$J = \sum_{i<j} u(r_{ij}) + \sum_{i} \sum_{\alpha} v(r_{i\alpha}) + \sum_{i<j} \sum_{\alpha} w(r_{ij}, r_{i\alpha}, r_{j\alpha})$$

where $r_{ij} = |r_i - R_\alpha|$, and $r_{i\alpha} = |r_i - R_\alpha|$. Various forms for the functions u,v, and w have been tested. For example, the minimal Padé form for u

$$u(r_{ij}) = \frac{a r_{ij}}{1 + b r_{ij}}.$$

But many other forms, see appendix H.

The trial wavefunction optimization

Aim: To find the "best" parameters of the trial wavefunction

- Minimization of the variational energy

$$E(\mathbf{p}) = \frac{\langle \Psi_T | H | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}$$

where $\mathbf{p}$ denotes the set of parameters of $\Psi_T(\mathbf{x}, \mathbf{p})$

- Minimization of the variance of the Hamiltonian

$$\sigma^2(\mathbf{p}) = \frac{\langle \Psi_T | [H - E(\mathbf{p})]^2 | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle}$$

Motivations:

- Reduce the statistical fluctuations (remember the zero-variance property)
- Reduce the fixed-node error

The Diffusion Monte Carlo (DMC) method

Very similar to the method presented above. It differs only in the way the local energy term in the diffusion equation is taken into account.

$$\boxed{\frac{\partial f(\mathbf{x},t)}{\partial t} = \frac{1}{2}\nabla^2 f(\mathbf{x},t) - \nabla[\mathbf{b}(\mathbf{x})f(\mathbf{x},t)] - (E_L(\mathbf{x}) - E_T)f(\mathbf{x},t)}$$

The equation of evolution of the local energy part is given by

$$\frac{\partial f(\mathbf{x},t)}{\partial t} = -(E_L(\mathbf{x}) - E_T)f(\mathbf{x},t)$$

whose solution is

$$f(\mathbf{x},t) = f(\mathbf{x},t=0)e^{-t(E_L(\mathbf{x})-E_T)}$$

Instead of considering $e^{-t(E_L(\mathbf{x})-E_T)}$ as a weight for the drifted brownian trajectories, we simulate this term as a **birth-death process or branching process.**

In the branching process the variation of density is reproduced by **killing or duplicating a certain number of times each walker** at position $\mathbf{x}$ proportionally to $e^{-t(E_L(\mathbf{x})-E_T)}$
The stationary density is now

$$\boxed{\pi_{DMC} = \Psi_T \Phi_0} \tag{4}$$

when E_T has ben taken equal to E_0.
The energy can be computed as

$$E_0 = \frac{\int \Phi_0 H \Psi_T}{\int \Phi_0 \Psi_T} = \frac{\int \Phi_0 \Psi_T \frac{H\Psi_T}{\Psi_T}}{\int \Phi_0 \Psi_T}$$

and then

$$\boxed{E_0 = \int d\mathbf{x} \pi_{DMC}(\mathbf{x}) E_L(\mathbf{x})} \tag{5}$$