

# Introduction to quantum Monte Carlo methods

Claudia Filippi, Ravindra Shinde, Stuart Shepard, Edgar Landinez

MESA+ Institute for Nanotechnology, Universiteit Twente, The Netherlands

Anthony Scemama

Laboratoire de Chimie et Physique Quantique, CNRS, Toulouse, France



## Monte Carlo methods

Approaches which make repeated use of random numbers:

- ▶ to simulate truly stochastic events
- ▶ to solve deterministic problems using probabilities

Very important class of methods in statistical mechanics

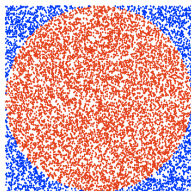
→ Sampling Boltzmann distribution

Computation of averages (integrals in many dimensions)

For quantum mechanical simulations → Quantum Monte Carlo

## A simple example of a Monte Carlo simulation

Basic idea of Monte Carlo through the “dartboard method”



→ Throw darts, compute  $A_{\text{circle}}$ , compute  $\pi$

Throw darts which land randomly within the square

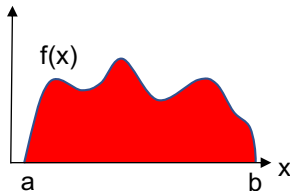
$$\frac{\# \text{ hits inside circle}}{\# \text{ hits inside the square}} = \frac{A_{\text{circle}}}{A_{\text{square}}} = \frac{\pi}{4}$$

↑  
many, many hits

## Monte Carlo integration

(1)

We want to compute the integral of  $f(x)$  in the interval  $[a, b]$



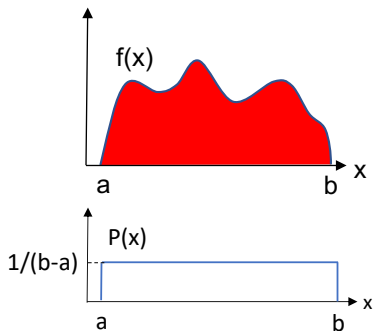
$$\begin{aligned} I &= \int_a^b f(x) dx = (b-a) \int_a^b f(x) \frac{1}{b-a} dx \\ &= (b-a) \langle f \rangle_{[a,b]} \end{aligned}$$

where  $\langle f \rangle_{[a,b]}$  is the average of the function in the range  $[a, b]$

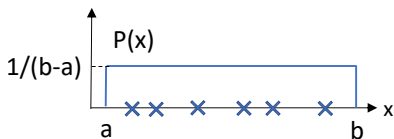
## Monte Carlo integration

(2)

$$\begin{aligned}\langle f \rangle_{[a,b]} &= \int_a^b f(x) \frac{1}{b-a} dx \\ &= \int_a^b f(x) P(x) dx\end{aligned}$$



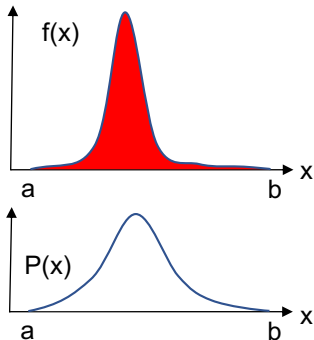
Draw  $M$  random numbers distributed uniformly in  $[a, b]$



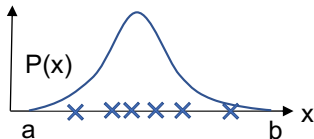
$$\langle f \rangle_{[a,b]} \approx \frac{1}{M} \sum_{i=1}^M f(x_i)$$

## A less uniform function

$$\begin{aligned} I &= \int_a^b f(x) dx \\ &= \int_a^b \frac{f(x)}{P(x)} P(x) dx \end{aligned}$$



Draw  $M$  random numbers distributed as  $P(x)$



$$\longrightarrow I \approx \frac{1}{M} \sum_{i=1}^M \frac{f(x_i)}{P(x_i)}$$

## Monte Carlo integration in a nutshell

We want to compute

$$\langle A \rangle = \int_a^b A(x)P(x)$$

with

$$P(x) \geq 0 \text{ and } \int_a^b P(x) = 1$$

← a probability density!

Monte Carlo → Sample  $\{x_1, \dots, x_M\}$  from  $P(x)$

$$\text{Estimate } \langle A \rangle \approx \frac{1}{M} \sum_{i=1}^M A(x_i)$$

Statistical physics:  $P(x) = \frac{e^{-\beta E(x)}}{Z}$ , the Boltzman distribution

## Quantum mechanical simulations

- Density functional theory methods

Large systems but approximate exchange/correlation

- Quantum chemistry post-Hartree-Fock methods

Accurate on small-medium systems

→ Jungle of approaches: CI, MCSCF, CC, CASPT2 ...

- Quantum Monte Carlo techniques

Stochastic solution of the Schrödinger equation

Accurate correlated calculations for medium-large systems



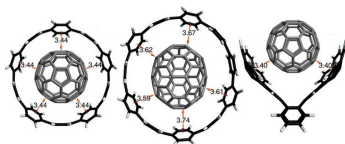
## Some general words about quantum Monte Carlo methods

Stochastically solve interacting Schrödinger equation

Why (real-space) quantum Monte Carlo?

- Favorable scaling  $\rightarrow$  Energy is  $O(N^4)$
- Flexibility in choice of functional form of wave function
- Easy parallelization
- Among most accurate calculations for medium-large systems

Routinely, molecules of up to 100 (mainly 1st/2nd-row) atoms



upto  $C_{136}H_{44}$  (Alfé 2017)

## A different way of writing the expectation values

Consider the expectation value of the Hamiltonian on  $\Psi$

$$\begin{aligned} E_V &= \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\int d\mathbf{R} \Psi^*(\mathbf{R}) \mathcal{H} \Psi(\mathbf{R})}{\int d\mathbf{R} \Psi^*(\mathbf{R}) \Psi(\mathbf{R})} \geq E_0 \\ &= \int d\mathbf{R} \frac{\mathcal{H} \Psi(\mathbf{R})}{\Psi(\mathbf{R})} \boxed{\frac{|\Psi(\mathbf{R})|^2}{\int d\mathbf{R} |\Psi(\mathbf{R})|^2}} \\ &= \int d\mathbf{R} E_L(\mathbf{R}) P(\mathbf{R}) = \langle E_L(\mathbf{R}) \rangle_P \end{aligned}$$

$P(\mathbf{R})$  is a probability density and  $E_L(\mathbf{R}) = \frac{\mathcal{H} \Psi(\mathbf{R})}{\Psi(\mathbf{R})}$  the local energy

## Variational Monte Carlo

Use Monte Carlo integration to compute expectation values

- ▷ Sample  $\mathbf{R}$  from  $P(\mathbf{R})$  using Metropolis algorithm
- ▷ Average local energy  $E_L(\mathbf{R}) = \frac{\mathcal{H}\Psi(\mathbf{R})}{\Psi(\mathbf{R})}$  to obtain  $E_V$  as

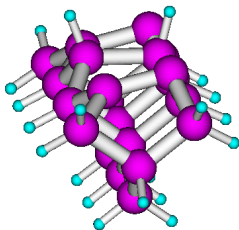
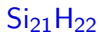
$$E_V = \langle E_L(\mathbf{R}) \rangle_P \approx \frac{1}{M} \sum_{i=1}^M E_L(\mathbf{R}_i)$$



Random walk in  $3N$  dimensions,  $\mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$

Just a **trick** to evaluate integrals in many dimensions

Is it really “just” a trick?



Number of electrons  $4 \times 21 + 22 = 106$

Number of dimensions  $3 \times 106 = 318$

Integral on a grid with 10 points/dimension  $\rightarrow 10^{318}$  points!

MC is a powerful trick  $\Rightarrow$  Freedom in form of the wave function  $\Psi$

## Monte Carlo integration

We want to compute an integral

$$E_V = \int d\mathbf{R} E_L(\mathbf{R}) P(\mathbf{R})$$

We sample  $P(\mathbf{R}) \rightarrow$   $E_V = \langle E_L(\mathbf{R}) \rangle_P \approx \frac{1}{M} \sum_{i=1}^M E_L(\mathbf{R}_i)$

- Does the trick always work?
- How efficient is it?

## The Central Limit Theorem

Probability density  $P$  and function  $f$  with finite mean and variance

$$\boxed{\mu} = \int dx f(x)P(x) \quad \boxed{\sigma^2} = \int dx (f(x) - \mu)^2 P(x)$$

Sample  $M$  independent random variables  $x_1, \dots, x_M$  from  $P(x)$

Define

$$F_M = \frac{1}{M} \sum_{i=1}^M f(x_i)$$

As  $M$  increases,  $F_M$  is normally distributed as  $\frac{1}{\sqrt{2\pi}\sigma} e^{-(x-\mu)^2/2\sigma^2}$

with a mean  $\boxed{\mu}$  and variance  $\boxed{\sigma_M^2 = \sigma^2/M}$

→ Irrespective of the original probability density function

## Conditions on many-body $\Psi$ to be used in VMC

Within VMC, we can use any “computable” wave function if

- ▷ Continuous, normalizable, proper symmetry
- ▷ Finite variance

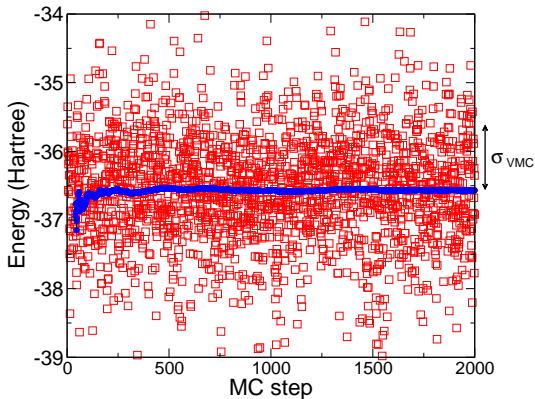
$$\sigma^2 = \frac{\langle \Psi | (\mathcal{H} - E_V)^2 | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle (E_L(\mathbf{R}) - E_V)^2 \rangle_P$$

since the Monte Carlo error goes as  $\text{err}(E_V) \sim \frac{\sigma}{\sqrt{M}}$

Zero variance principle: if  $\Psi \rightarrow \Psi_0$ ,  $E_L(\mathbf{R})$  does not fluctuate

## Typical VMC run

Example: Local energy and average energy of acetone ( $\text{C}_3\text{H}_6\text{O}$ )



$$E_{\text{VMC}} = \langle E_{\text{L}}(\mathbf{R}) \rangle_P = -36.542 \pm 0.001 \text{ Hartree (40} \times 20000 \text{ steps)}$$

$$\sigma_{\text{VMC}} = \langle (E_{\text{L}}(\mathbf{R}) - E_{\text{VMC}})^2 \rangle_P = 0.90 \text{ Hartree}$$



## Variational Monte Carlo: To do list

- Method to sample distribution function  $P(\mathbf{R}) = \frac{|\Psi(\mathbf{R})|^2}{\int d\mathbf{R} |\Psi(\mathbf{R})|^2}$

→ Obtain a set of  $\{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M\}$  distributed as  $P(\mathbf{R})$

How? As in classical Monte Carlo with Metropolis algorithm!

- Build the wave function  $\Psi(\mathbf{R})$ . Which functional form ?

Here, we spend most of our time, open topic of research

- Compute expectation values  $\frac{\langle \Psi | \mathcal{O} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$

Reformulate them to reduce fluctuations, open topic of research

How do we sample  $P(\mathbf{R})$ ?

Generate a Markov chain

$$\dots \xrightarrow{M} \mathbf{R} \xrightarrow{M} \mathbf{R}' \xrightarrow{M} \mathbf{R}'' \xrightarrow{M} \dots$$



Construct  $M(\mathbf{R}_f|\mathbf{R}_i)$  as probability for transition  $\mathbf{R}_i \rightarrow \mathbf{R}_f$  so that

- $M(\mathbf{R}_f|\mathbf{R}_i) \geq 0$  and  $\int d\mathbf{R}_f M(\mathbf{R}_f|\mathbf{R}_i) = 1$  (stochastic)
- If we start from an arbitrary distribution  $P_{\text{init}}$ , we evolve to  $P$   
→ Impose stationarity condition

## Constructing $M$

To sample  $P$ , use  $M$  which satisfies **stationarity condition**:

$$\int d\mathbf{R}_i M(\mathbf{R}_f | \mathbf{R}_i) P(\mathbf{R}_i) = P(\mathbf{R}_f) \quad \forall \mathbf{R}_f$$

▷ Stationarity condition

⇒ If we start with  $P$ , we continue to sample  $P$

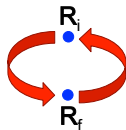
▷ Stationarity condition + stochastic property of  $M$  + ergodicity

⇒ Any initial distribution will evolve to  $P$

More stringent condition

In practice, we impose detailed balance condition

$$M(\mathbf{R}_f|\mathbf{R}_i) P(\mathbf{R}_i) = M(\mathbf{R}_i|\mathbf{R}_f) P(\mathbf{R}_f)$$



Stationarity condition can be obtained by summing over  $\mathbf{R}_i$

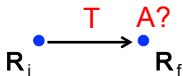
$$\int d\mathbf{R}_i M(\mathbf{R}_f|\mathbf{R}_i) P(\mathbf{R}_i) = \underbrace{\int d\mathbf{R}_i M(\mathbf{R}_i|\mathbf{R}_f) P(\mathbf{R}_f)}_1 = P(\mathbf{R}_f)$$

Detailed balance is a sufficient but not necessary condition

How do we construct the transition matrix  $P$  in practice?

Metropolis method  $\rightarrow$  Write  $M$  as proposal  $T \times$  acceptance  $A$

$$M(\mathbf{R}_f|\mathbf{R}_i) = A(\mathbf{R}_f|\mathbf{R}_i) T(\mathbf{R}_f|\mathbf{R}_i)$$



Let us rewrite the detailed balance condition

$$M(\mathbf{R}_f|\mathbf{R}_i) P(\mathbf{R}_i) = M(\mathbf{R}_i|\mathbf{R}_f) P(\mathbf{R}_f)$$

$$A(\mathbf{R}_f|\mathbf{R}_i) T(\mathbf{R}_f|\mathbf{R}_i) P(\mathbf{R}_i) = A(\mathbf{R}_i|\mathbf{R}_f) T(\mathbf{R}_i|\mathbf{R}_f) P(\mathbf{R}_f)$$

$$\Rightarrow \frac{A(\mathbf{R}_f|\mathbf{R}_i)}{A(\mathbf{R}_i|\mathbf{R}_f)} = \frac{T(\mathbf{R}_i|\mathbf{R}_f) P(\mathbf{R}_f)}{T(\mathbf{R}_f|\mathbf{R}_i) P(\mathbf{R}_i)}$$

## Choice of acceptance matrix $A$

Original choice by Metropolis *et al.* maximizes the acceptance

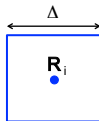
$$A(\mathbf{R}_f|\mathbf{R}_i) = \min \left\{ 1, \frac{T(\mathbf{R}_i|\mathbf{R}_f) P(\mathbf{R}_f)}{T(\mathbf{R}_f|\mathbf{R}_i) P(\mathbf{R}_i)} \right\}$$

Note:  $P(\mathbf{R})$  does not have to be normalized

→ For complicated  $\Psi$  we do not know the normalization!

→  $P(\mathbf{R}) = |\Psi(\mathbf{R})|^2$

## Original Metropolis method



Symmetric  $T(\mathbf{R}_f|\mathbf{R}_i) = 1/\Delta^{3N} \Rightarrow A(\mathbf{R}_f|\mathbf{R}_i) = \min \left\{ 1, \frac{P(\mathbf{R}_f)}{P(\mathbf{R}_i)} \right\}$

Better choices of proposal matrix  $T$

Sequential correlation  $\Rightarrow M_{\text{eff}} < M$  independent observations

$$M_{\text{eff}} = \frac{M}{T_{\text{corr}}} \quad \text{with } T_{\text{corr}} \text{ autocorrelation time of desired observable}$$

Aim is to achieve fast evolution and reduce correlation times

Use freedom in choice of  $T$ : For example, use available trial  $\Psi$

$$T(\mathbf{R}_f | \mathbf{R}_i) = \mathcal{N} \exp \left[ -\frac{(\mathbf{R}_f - \mathbf{R}_i - \mathbf{V}(\mathbf{R}_i)\tau)^2}{2\tau} \right] \quad \text{with } \mathbf{V}(\mathbf{R}_i) = \frac{\nabla \Psi(\mathbf{R}_i)}{\Psi(\mathbf{R}_i)}$$

## Summary of variational Monte Carlo

Interested for instance in expectation value of Hamiltonian on  $\Psi$

$$E_V = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \int d\mathbf{R} \frac{\mathcal{H}\Psi(\mathbf{R})}{\Psi(\mathbf{R})} \frac{|\Psi(\mathbf{R})|^2}{\int d\mathbf{R} |\Psi(\mathbf{R})|^2} = \int d\mathbf{R} E_L(\mathbf{R}) P(\mathbf{R})$$

Use Metropolis algorithm to obtain  $M$  samples distributed as  $P(\mathbf{R})$

→ Estimate  $E_V$  and  $\sigma$  as

$$E_V = \int d\mathbf{R} E_L(\mathbf{R}) P(\mathbf{R}) \quad \rightarrow \quad \bar{E}_V = \frac{1}{M} \sum_{i=1}^M E_L(\mathbf{R}_i)$$

$$\sigma^2 = \int d\mathbf{R} (E_L(\mathbf{R}) - E_V)^2 P(\mathbf{R}) \quad \rightarrow \quad \bar{\sigma}^2 = \frac{1}{M} \sum_{i=1}^M (E_L(\mathbf{R}_i) - \bar{E}_V)^2$$

Compute error: Samples are correlated → blocking (see tutorial)



Variational Monte Carlo  $\rightarrow$  Freedom in choice of  $\Psi$

Monte Carlo integration allows the use of complex and accurate  $\Psi$

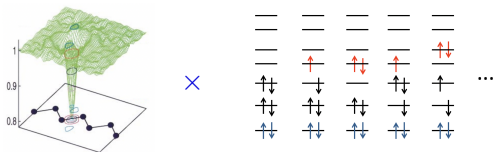
$\Rightarrow$  More compact representation of  $\Psi$  than in quantum chemistry

$\Rightarrow$  Beyond  $c_0 D_{\text{HF}} + c_1 D_1 + c_2 D_2 + \dots$  millions of determinants

## Jastrow-Slater wave function

Commonly employed compact Jastrow-Slater wave functions

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \mathcal{J}(\mathbf{r}_1, \dots, \mathbf{r}_N) \times \sum_i c_i D_i(\mathbf{r}_1, \dots, \mathbf{r}_N)$$



$\mathcal{J}$   $\longrightarrow$  Jastrow correlation factor

– Explicit dependence on electron-electron distances  $r_{ij}$

$\sum_i c_i D_i$   $\longrightarrow$  Determinants of single-particle orbitals

– Few and not millions of determinants

## Jastrow factor and divergences in the potential

At interparticle coalescence points, the potential diverges as

$$-\frac{Z}{r_{i\alpha}} \quad \text{for the electron-nucleus potential}$$

$$\frac{1}{r_{ij}} \quad \text{for the electron-electron potential}$$

Local energy  $\frac{\mathcal{H}\Psi}{\Psi} = -\frac{1}{2} \sum_i \frac{\nabla_i^2 \Psi}{\Psi} + \mathcal{V}$  must be finite

$\Rightarrow$  Kinetic energy must have opposite divergence to the potential  $\mathcal{V}$

## Divergence in potential and Kato's cusp conditions

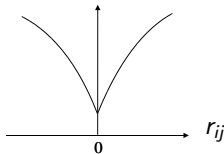
Finite local energy as  $r_{ij} \rightarrow 0 \Rightarrow \Psi$  must satisfy:

$$\left. \frac{\partial \Psi}{\partial r_{ij}} \right|_{r_{ij}=0} = \mu_{ij} q_i q_j \Psi(r_{ij} = 0)$$

Electron-electron cusps imposed through the Jastrow factor

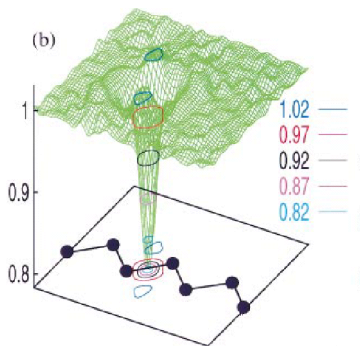
Example: Simple Jastrow factor  $\rightarrow \mathcal{J}(r_{ij}) = \prod_{i < j} \exp \left\{ b_0 \frac{r_{ij}}{1 + b r_{ij}} \right\}$

Imposes cusp conditions  
+  
keeps electrons apart



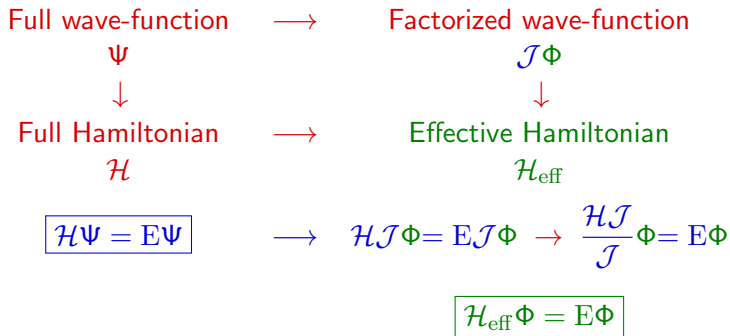
## The effect of the Jastrow factor

Pair correlation function for  $\uparrow\downarrow$  electrons in the (110) plane of Si  
 $g_{\uparrow\downarrow}(\mathbf{r}, \mathbf{r}')$  with one electron is at the bond center



Hood *et al.* Phys. Rev. Lett. **78**, 3350 (1997)

Why should  $\Psi_{\text{QMC}} = \mathcal{J}D$  work?



$\mathcal{H}_{\text{eff}}$  weaker Hamiltonian than  $\mathcal{H}$

$\Rightarrow$   $\Phi \approx$  non-interacting wave function  $D$

$\Rightarrow$  Quantum Monte Carlo wave function  $\Psi = \mathcal{J}D$

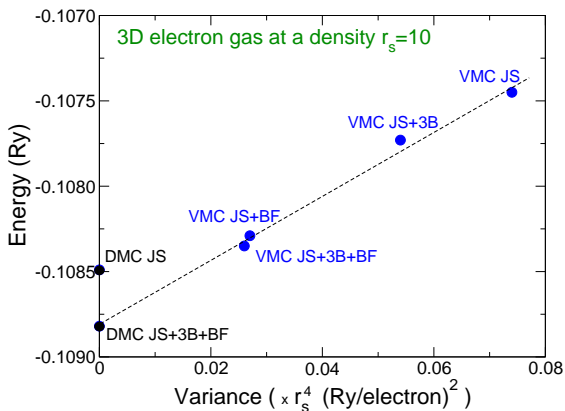
## Beyond VMC?

Removing or reducing wave function bias?

⇒ Projection Monte Carlo methods

## Why going beyond VMC?

### Dependence of VMC from wave function $\Psi$



Kwon, Ceperley, Martin, Phys. Rev. B **58**, 6800 (1998)



## Why going beyond VMC?

What goes in, comes out! Can we remove wave function bias?

## Projector (diffusion) Monte Carlo method

- ▷ Construct an operator which inverts spectrum of  $\mathcal{H}$

$$\boxed{\text{Diffusion Monte Carlo}} \rightarrow e^{-\tau(\mathcal{H}-E_{\text{ref}})}$$

- ▷ Use it to stochastically project the ground state of  $\mathcal{H}$

## Diffusion Monte Carlo

Consider initial guess  $\Psi^{(0)}$  and repeatedly apply projection operator

$$\Psi^{(n)} = e^{-\tau(\mathcal{H}-E_{\text{ref}})}\Psi^{(n-1)}$$

Expand  $\Psi^{(0)}$  on the eigenstates  $\Psi_i$  with energies  $E_i$  of  $\mathcal{H}$

$$\Psi^{(n)} = e^{-n\tau(\mathcal{H}-E_{\text{ref}})}\Psi^{(0)} = \sum_i \Psi_i \langle \Psi_i | \Psi^{(0)} \rangle e^{-n\tau(E_i-E_{\text{ref}})}$$

and obtain in the limit of  $n \rightarrow \infty$

$$\lim_{n \rightarrow \infty} \Psi^{(n)} = \Psi_0 \langle \Psi_0 | \Psi^{(0)} \rangle e^{-n\tau(E_0-E_{\text{ref}})}$$

If we choose  $E_{\text{ref}} \approx E_0$ , we obtain

$$\lim_{n \rightarrow \infty} \Psi^{(n)} = \Psi_0$$

How do we perform the projection?

Rewrite projection equation in integral form

$$\Psi(\mathbf{R}', t + \tau) = \int d\mathbf{R} G(\mathbf{R}', \mathbf{R}, \tau) \Psi(\mathbf{R}, t)$$

where  $G(\mathbf{R}', \mathbf{R}, \tau) = \langle \mathbf{R}' | e^{-\tau(\mathcal{H} - E_{\text{ref}})} | \mathbf{R} \rangle$

▷ Can we sample the wave function?

For the moment, assume we are dealing with bosons, so  $\Psi > 0$

▷ Can we interpret  $G(\mathbf{R}', \mathbf{R}, \tau)$  as a transition probability?

If yes, we can perform this integral by Monte Carlo integration

## What we know about the Green's function

$$\Psi(t) = e^{-t(\mathcal{H}-E_T)}\Psi(0)$$

$\Psi(\mathbf{R}, t)$  satisfies the imaginary-time Schrödinger equation

$$(\mathcal{H} - E_{\text{ref}})\Psi(\mathbf{R}, t) = -\frac{\partial\Psi(\mathbf{R}, t)}{\partial t}$$

$$\Psi(\mathbf{R}, t) = \int d\mathbf{R}_0 G(\mathbf{R}, \mathbf{R}_0, t)\Psi^{(0)}(\mathbf{R}_0)$$

$G(\mathbf{R}', \mathbf{R}, t)$  satisfies the imaginary-time Schrödinger equation

$$(\mathcal{H} - E_{\text{ref}})G(\mathbf{R}, \mathbf{R}_0, t) = -\frac{\partial G(\mathbf{R}, \mathbf{R}_0, t)}{\partial t}$$

with  $G(\mathbf{R}', \mathbf{R}, t) = \langle \mathbf{R}' | e^{-t(\mathcal{H}-E_T)} | \mathbf{R} \rangle$  and  $G(\mathbf{R}', \mathbf{R}, 0) = \delta(\mathbf{R}' - \mathbf{R})$

Can we interpret  $G(\mathbf{R}', \mathbf{R}, \tau)$  as a transition probability?

(1)

$$\mathcal{H} = \mathcal{T}$$

Imaginary-time Schrödinger equation is a diffusion equation

$$-\frac{1}{2}\nabla^2 G(\mathbf{R}, \mathbf{R}_0, t) = -\frac{\partial G(\mathbf{R}, \mathbf{R}_0, t)}{\partial t}$$

The Green's function is given by a Gaussian

$$G(\mathbf{R}', \mathbf{R}, \tau) = (2\pi\tau)^{-3N/2} \exp\left[-\frac{(\mathbf{R}' - \mathbf{R})^2}{2\tau}\right]$$

Positive and can be sampled

Can we interpret  $G(\mathbf{R}', \mathbf{R}, \tau)$  as a transition probability? (2)

$$\mathcal{H} = \mathcal{V}$$

$$(\mathcal{V}(\mathbf{R}) - E_{\text{ref}})G(\mathbf{R}, \mathbf{R}_0, t) = -\frac{\partial G(\mathbf{R}, \mathbf{R}_0, t)}{\partial t},$$

The Green's function is given by

$$G(\mathbf{R}', \mathbf{R}, \tau) = \exp[-\tau(\mathcal{V}(\mathbf{R}) - E_{\text{ref}})] \delta(\mathbf{R} - \mathbf{R}'),$$

Positive but does not preserve the normalization

It is a factor by which we multiply the distribution  $\Psi(\mathbf{R}, t)$

$\mathcal{H} = \mathcal{T} + \mathcal{V}$  and a combination of diffusion and branching

Let us combine previous results

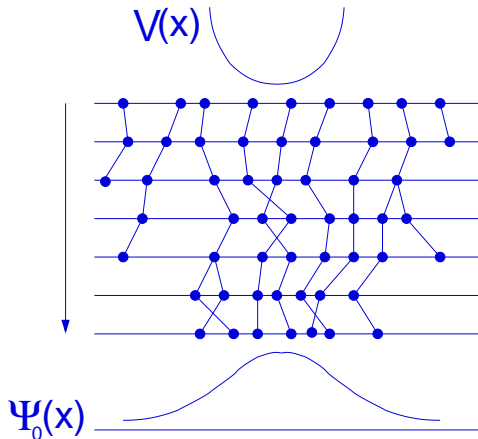
$$G(\mathbf{R}', \mathbf{R}, \tau) \approx (2\pi\tau)^{-3N/2} \exp\left[-\frac{(\mathbf{R}' - \mathbf{R})^2}{2\tau}\right] \exp[-\tau(\mathcal{V}(\mathbf{R}) - E_T)]$$

Diffusion + branching factor leading to survival/death/cloning

Why? Trotter's theorem  $\rightarrow e^{(A+B)\tau} = e^{A\tau} e^{B\tau} + \mathcal{O}(\tau^2)$

$\rightarrow$  Green's function in the short-time approximation to  $\mathcal{O}(\tau^2)$

## Diffusion and branching in a harmonic potential

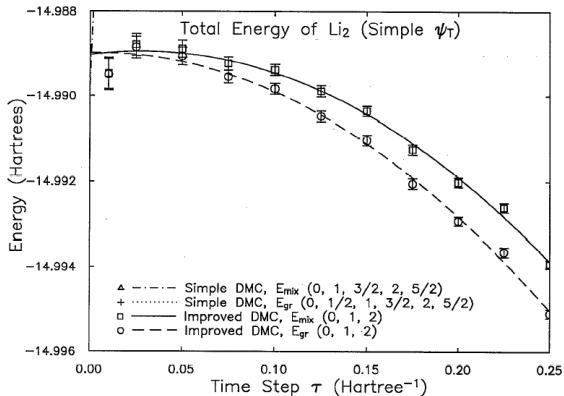


Walkers proliferate/die where potential is lower/higher than  $E_{\text{ref}}$



## Time-step extrapolation

Example: Energy of  $\text{Li}_2$  versus time-step  $\tau$

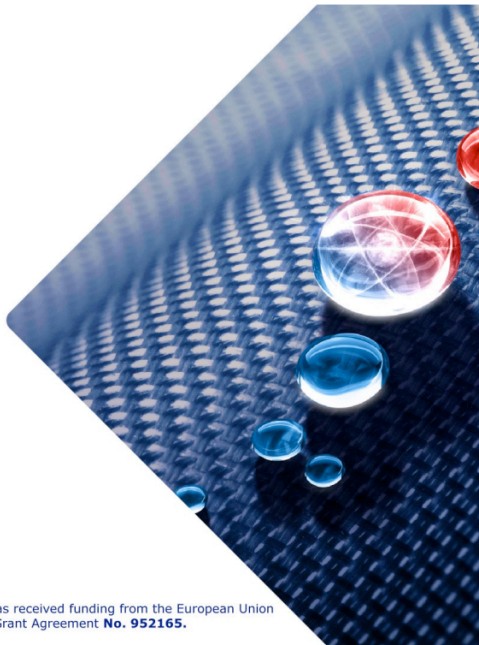


Umrigar, Nightingale, Runge, J. Chem. Phys. **94**, 2865 (1993)

## Problems with simple algorithm

The simple algorithm is inefficient and unstable

- ▷ Potential can vary a lot and be unbounded  
e.g. electron-nucleus interaction → Exploding population
- ▷ Branching factor grows with system size



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