Monte Carlo simulations in physics: quantum Monte Carlo

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Learning objectives

- Case study of many-body quantum simulation: Interacting particles in a harmonic oscillator studied using Variational (Quantum) Monte Carlo
- VMC wave function ansatz and parameter optimisation

Some preliminaries

- Schrödinger equation (mostly the time-independent version)
- Basic ideas of quantum statistics (bosons vs fermions)
- The variational principle in quantum mechanics

The stationary many-body Schrödinger equation

$$\hat{H}\Psi_n = E_n\Psi_n, \text{ where}$$ (in Hartree atomic units)

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_i\sum_{j\neq i}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i V_{\text{ext}}(\mathbf{r}_i)$$

for like particles in external potential (unit charge, like for electrons), and

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N),$$

is a high-dimensional (3N) object.

Physical observables in quantum mechanics

- Values of physical observables can be calculated directly from the wave function

$$\langle O \rangle = \frac{\int \Psi^* \hat{O} \Psi d\mathbf{R}}{\int \Psi^* \Psi d\mathbf{R}}$$

- Here **R** contains all the particle coordinates $\mathbf{r}_1$, … $\mathbf{r}_N$

Wave function symmetry/ antisymmetry (”statistics”)

The probability density of a two-particle wave function of indistinguishable particles should not change when the particles are interchanged,

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\Psi(\mathbf{r}_2, \mathbf{r}_1)|^2$$

We can achieve this in two ways:

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

The particles whose wave functions are symmetric (”+” sign) under particle interchange have integral or zero intrinsic spin, and are termed bosons. Particles whose wave functions which are anti-symmetric (”-” sign) under particle interchange have half-integral intrinsic spin, and are termed fermions. Consider, what happens when the particles approach one another?

Wave function symmetry/ antisymmetry (”statistics”)

Consider a two-body noninteracting system. Let’s try to construct the system as a linear combination of products of two single particle wave functions (since particles are indistinguishable, we cannot know which term would describe the system)

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = A\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + B\psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)$$

There are only two correctly normalised combinations possible

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)]$$

In the case of Fermions (”-”), if *a=b*, then, $\Psi = 0$ implying that no two fermions can occupy the same state. Bosons do not obey this principle and many of them can be found in the lowest (ground) state. These properties result in Fermi-Dirac and Bose-Einstein statistics for non-interacting fermions and bosons, respectively.

Variational quantum Monte Carlo

Any wave function Ψ satisfies:

$$E_0 \leq E = \frac{\int \Psi^* H \Psi \, d\mathbf{R}}{\int \Psi^* \Psi \, d\mathbf{R}} \, ,$$

if it has correct particle statistics.

E_0 is the ground state energy.

The integrals are high-dimensional: $d \times N$, where

d is the dimension of the space and N number of particles

$\mathbf{R}$ contains all these coordinates.

Invent a wave function Ψ and calculate the energy as above.

Very simple!

Variational quantum Monte Carlo

We can use Monte Carlo integration with Metropolis sampling:

$$E = \frac{\int \Psi^* H \Psi \, d\mathbf{R}}{\int \Psi^* \Psi \, d\mathbf{R}} = \frac{\int |\Psi|^2 \frac{H\Psi}{\Psi} \, d\mathbf{R}}{\int |\Psi|^2 \, d\mathbf{R}} = \lim_{M\to\infty} \frac{1}{M} \sum_{i=1}^{M} E_L(\mathbf{R}_i) = \langle E_L \rangle_{|\Psi|^2} \, ,$$

where the local energy is

$$E_L = \frac{H\Psi}{\Psi}$$

Constant for exact eigenstates

and $\mathbf{R}_i$ is sampled from $|\Psi(\mathbf{R})|^2$.

If you have an analytic many-body wave function,
Monte Carlo is very good in extracting information out of it!

Warming up with harmonic oscillator

Hamiltonian:

$$H = -\frac{1}{2}\frac{d^2}{dx^2} + \frac{1}{2}x^2 \ ,$$

and trial wave function

$$\psi(x) = e^{-\alpha x^2} \ .$$

Local energy:

$$E_L = \frac{H\psi}{\psi} = -\frac{1}{2}\frac{d^2\psi}{dx^2}\frac{1}{\psi} + \frac{1}{2}x^2 = \alpha - 2\alpha^2 x^2 + \frac{1}{2}x^2 \ .$$

Notice that potential part in E_L is always simple: $\frac{V\psi}{\psi} = V$.

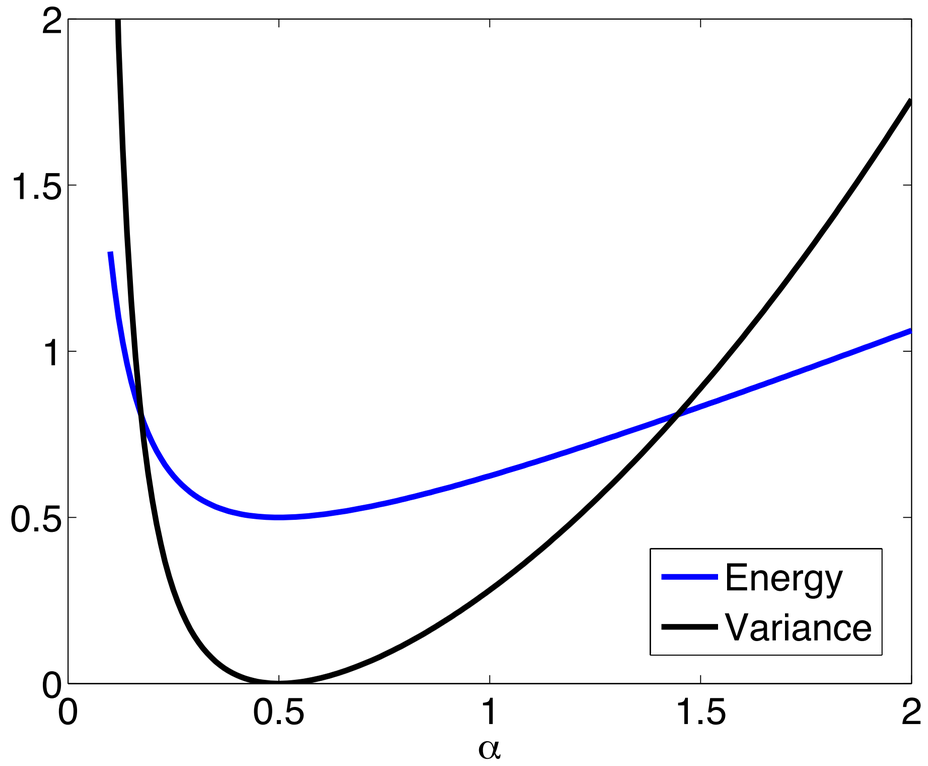
Gaussian integrals are doable: $\langle x^2 \rangle = \frac{\int x^2\psi^2}{\int \psi^2} = \frac{1}{4\alpha}$. So energy is $E(\alpha) = \frac{1}{8\alpha} + \frac{\alpha}{2}$.

Variance of local energy: $\sigma^2_{E_L} = \frac{(1-4\alpha^2)^2}{32\alpha^2}$

We use Monte Carlo for integrals later, as no analytic results for real problems!

Warming up with harmonic oscillator

Energy and variance as a function of the parameter in the wave function:



Both curves show a minimum at the same parameter value.

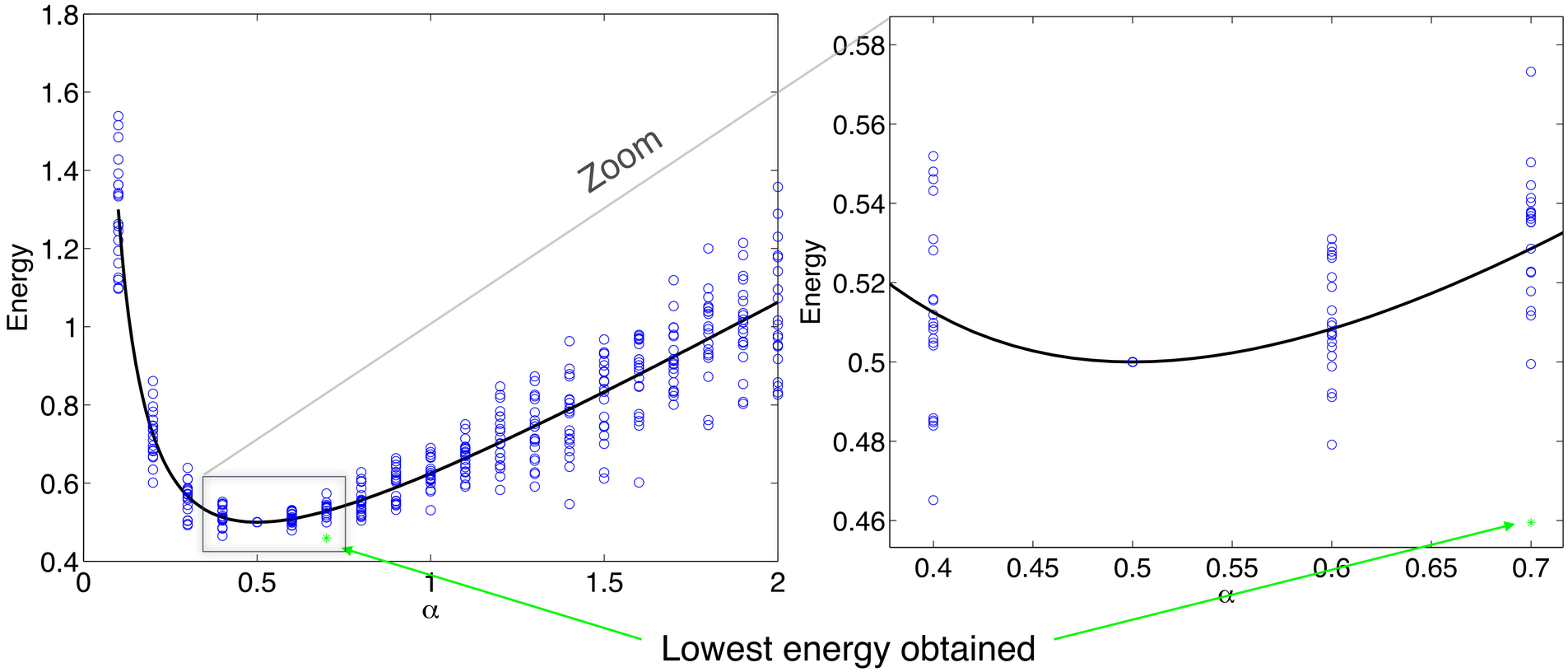
The variance is zero at that point.

These are the analytic results.

Warming up with harmonic oscillator

Calculating the energy stochastically, many simulations.

Sample coordinate from the density, and evaluate local energy, gives circles below.
Lines are the analytic results.



Stochastic noise make it somewhat hard to locate the minimum of energy.

You might think that the minimum is at 0.4 if you have only a few simulations.

Simplest VMC

Usually wave function contains tunable parameters α.

- Invent a many-body wave function Ψ with a few parameters.
- Calculate E.
- Vary components of α and locate minimum of energy.
- Calculate other observables with optimal parameters.

Very limited! Optimization is very slow.

We actually try to optimize a function $\lim_{M\to\infty} \frac{1}{M} \sum_{i=1}^{M} E_L(\mathbf{R}_i)$

For a finite M, cost function has noise:

Mathematically this is optimization of a noisy function.

Traditional optimizations methods typically fail.

Metropolis

The high-dimensional integrals again calculated using Monte Carlo.

N_W walkers perform N_S metropolis steps.

For each walker and step:

- Move the walker $\mathbf{R} \to \mathbf{R}'$ by e.g. moving one of particles.
- Calculate the ratio $p = |\Psi(\mathbf{R}')/\Psi(\mathbf{R})|^2$.
- Accept move if $p > r$ (r random number $[0, 1]$)
- Make measurements (like local energy).

Finish when observables are converged.

Walkers are uncorrelated, can be directly used for error estimate.

Energy derivative

Derivative of the energy with respect to one of the parameters.

Assume real Ψ, and denoting $\Psi' = \frac{\partial \Psi}{\partial \alpha}$ below.

$$
\begin{aligned}
\frac{\partial E}{\partial \alpha} &= \frac{\left(\int \Psi' H \Psi + \int \Psi H \Psi'\right) \int \Psi^2 - 2 \int \Psi' \Psi \int \Psi H \Psi}{\left(\int \Psi^2\right)^2} \\
&= \frac{2 \int \Psi^2 \frac{\Psi'}{\Psi} \frac{H\Psi}{\Psi}}{\int \Psi^2} - \frac{2 \int \Psi^2 \frac{\Psi'}{\Psi}}{\int \Psi^2} \frac{\int \Psi^2 \frac{H\Psi}{\Psi}}{\int \Psi^2} \\
&= 2 \left\langle \frac{\Psi'}{\Psi} \frac{H\Psi}{\Psi} \right\rangle - 2 \left\langle \frac{\Psi'}{\Psi} \right\rangle \left\langle \frac{H\Psi}{\Psi} \right\rangle \\
&= 2 \left\langle \frac{\Psi'}{\Psi} E_L \right\rangle - 2 \left\langle \frac{\Psi'}{\Psi} \right\rangle \langle E_L \rangle
\end{aligned}
$$

In $\langle \ldots \rangle$, $\mathbf{R}$ is sampled from Ψ^2.

If E_L is constant, derivative is zero.

Optimization in VMC

Sample $|\Psi(\mathbf{R}, \alpha_i)|^2$ with m walkers $\{\mathbf{R}_j\}_{j=1}^m$ using e.g. Metropolis algorithm.

Change parameters according to rule:

$$\alpha_{i+1} = \alpha_i - \gamma_i \nabla_\alpha E$$

where ∇-term is done as in previous page.

Gradient of energy with respect to parameters, now $\langle \ldots \rangle$ is an average over walkers.

γ_i is a damping factor, ensuring convergence.

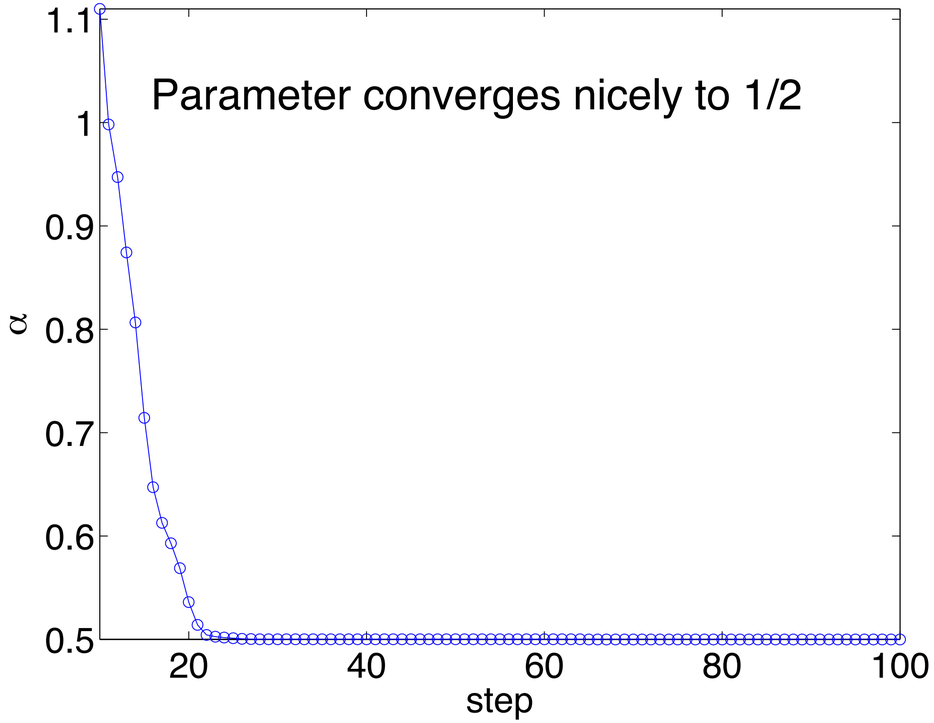
Parameters move to direction that lowers energy.

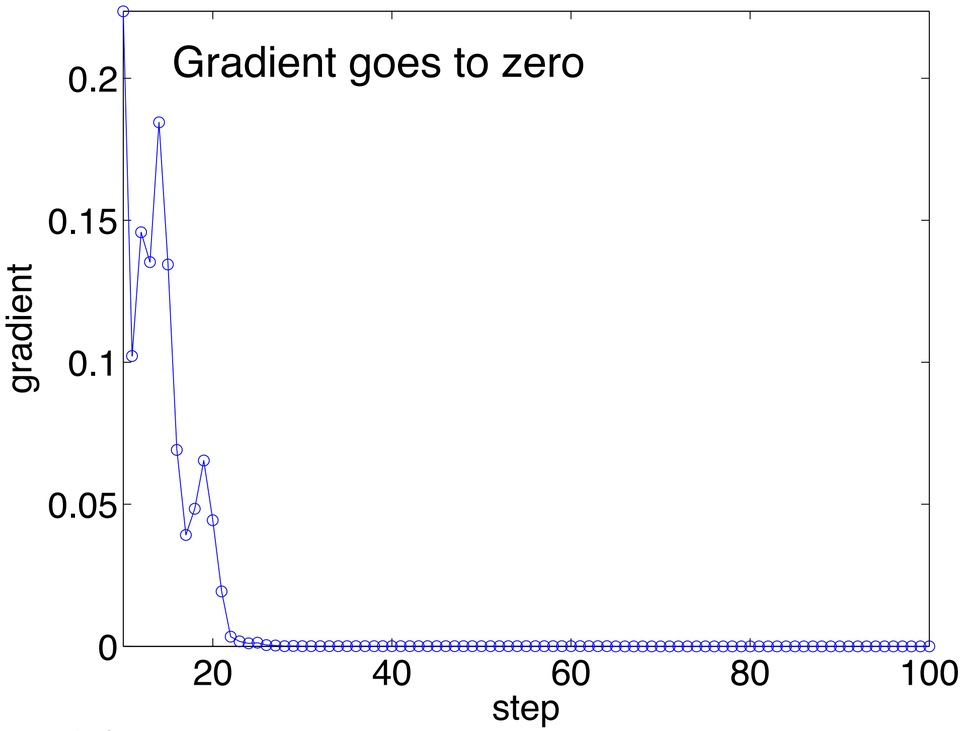
Walkers sample density (that changes).

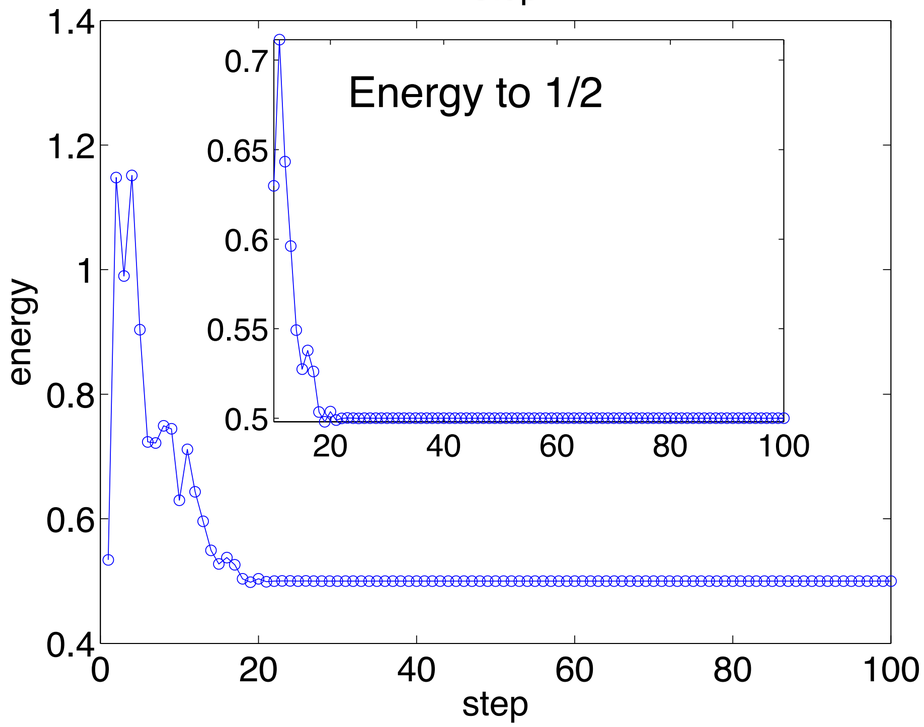
When converged, gradient is zero on average.

$\nabla_\alpha E$ still fluctuates (in typical cases).

VMC, pure harmonic



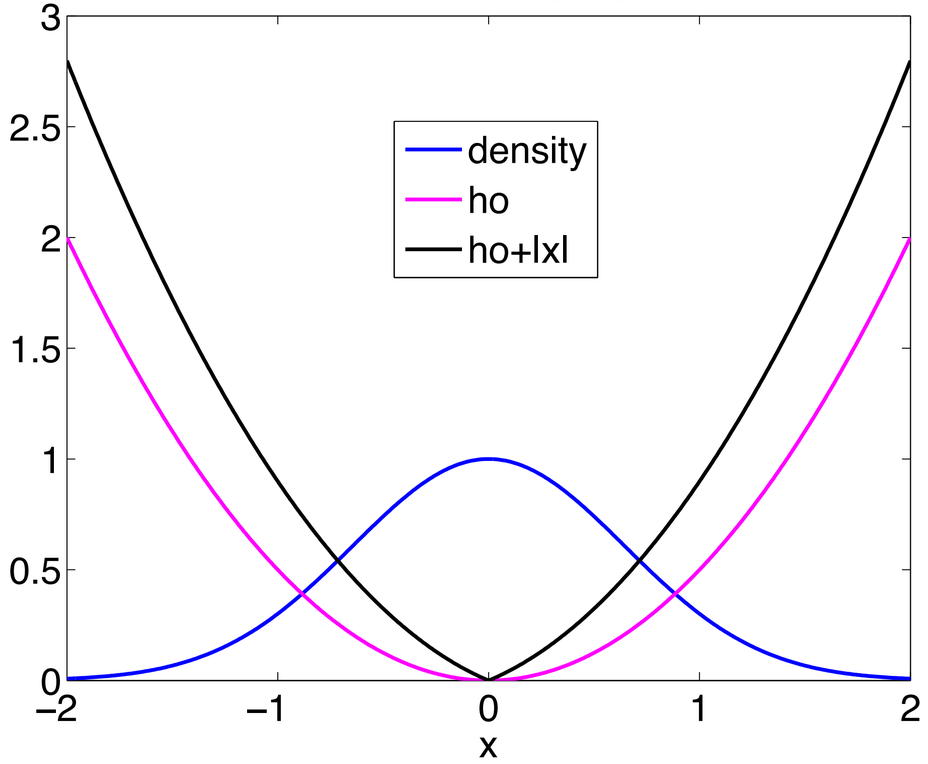


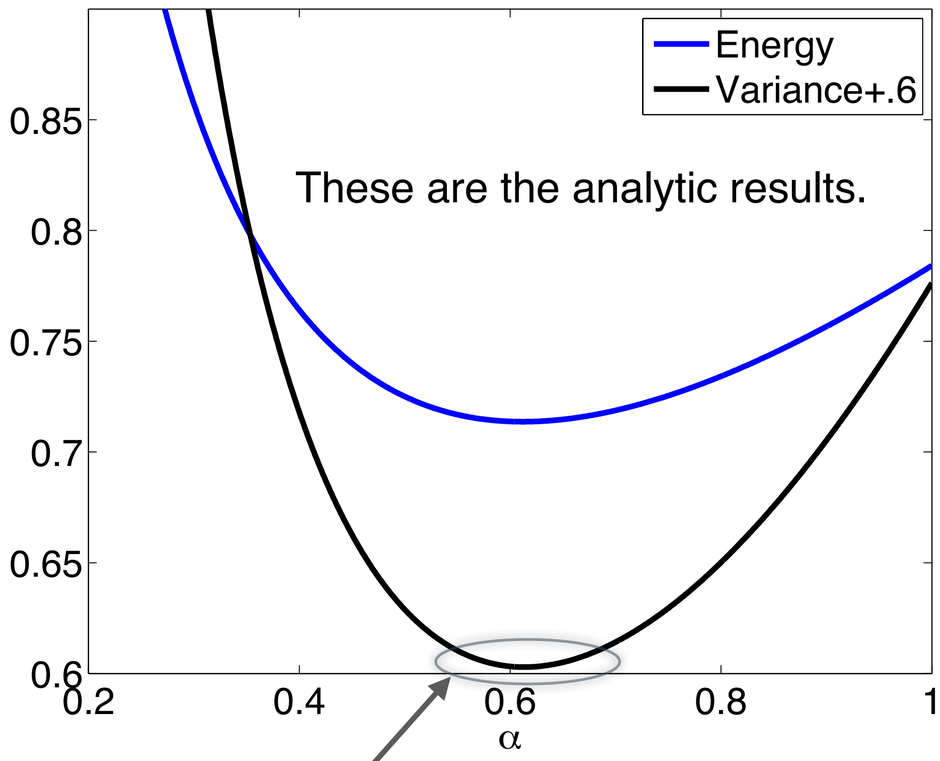


This is not a typical case, as the optimal wave function is the exact ground state to the problem.

Next, a more “typical” case…

Perturbing potential with |x|





Same trial wave function, gaussian.

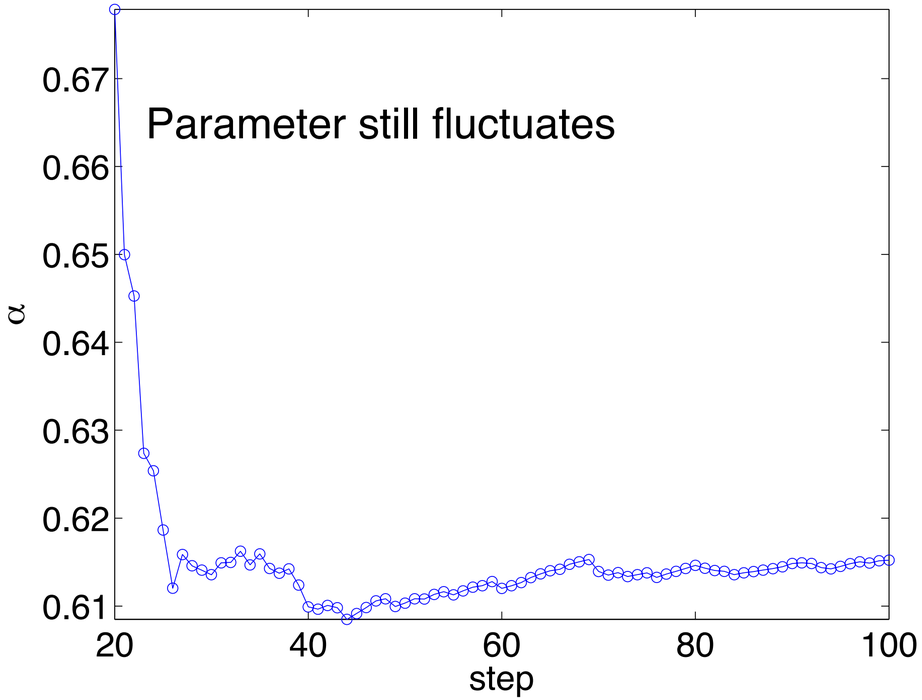
This does not solve the problem exactly anymore.

The variance is now finite even for the optimal parameter.

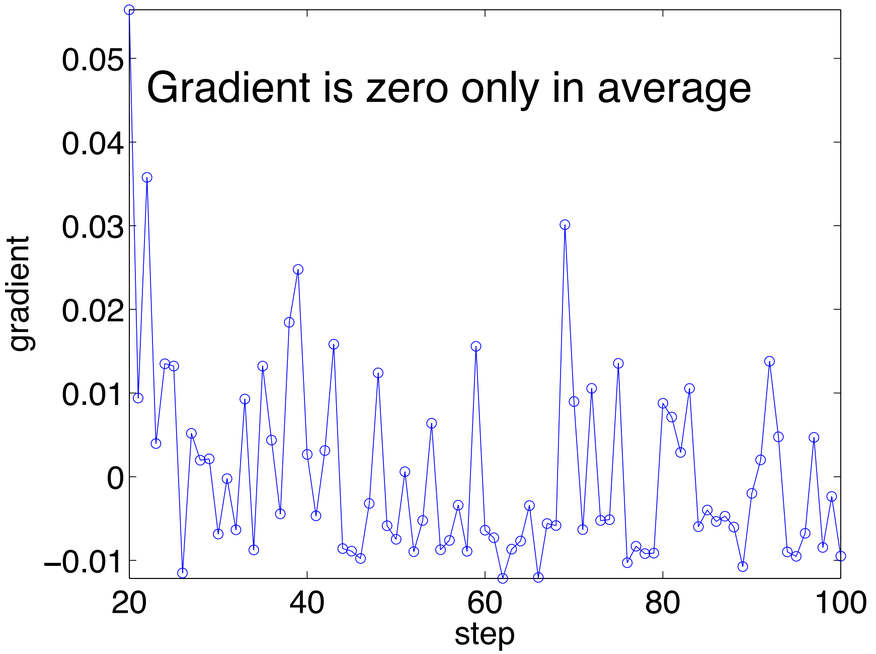
Strength of the linear term around 0.4 [actual value is 1/sqrt(2*pi) for simpler plotting].

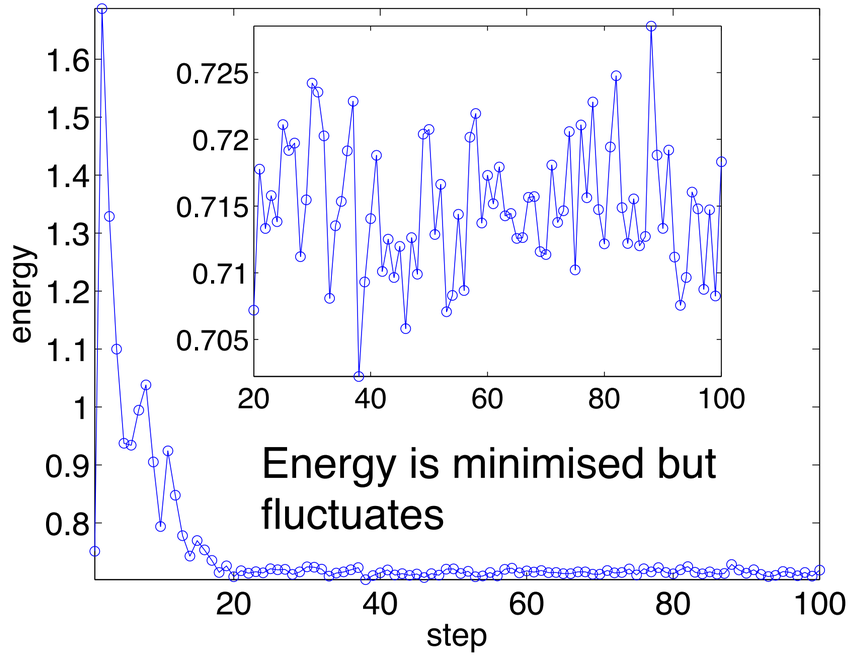
These are again analytic results, but we try to do the wave function optimisation now with a Monte Carlo technique.

VMC, |x|+harmonic



We see that the simulation reaches the correct parameter value range, and the gradient fluctuates around zero there.





Correlated fermion wave function

Very often used, simple generalization of Slater determinant:

$$\Psi(\mathbf{R}) = \det_{\uparrow}[\psi_i(\mathbf{r}_j)]\det_{\downarrow}[\psi_k(\mathbf{r}_l)] \prod_{i<j}^{N} J(r_{ij}) \ ,$$

where J is the Jastrow pair-correlation factor.

Has explicit dependence on the inter-electron distances, captures correlation.

Usually, both ψ and J have variational parameters.

Example: Two electrons in 2D ho

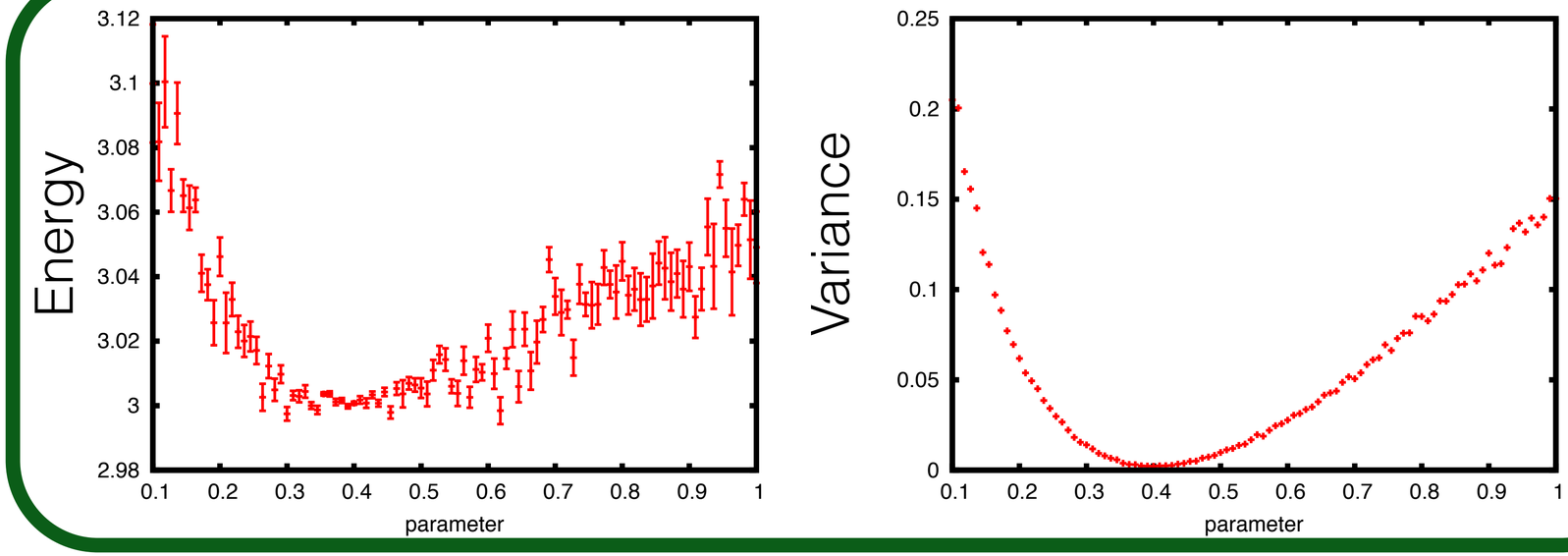
$$H = -\frac{1}{2}\sum_{i=1}^{2}(\nabla_i^2 - r_i^2) + \frac{1}{r_{12}} \ , \quad \psi = e^{-r_1^2/2}e^{-r_2^2/2}(1 + r_{12})$$

exact ground state with $E = 3$.

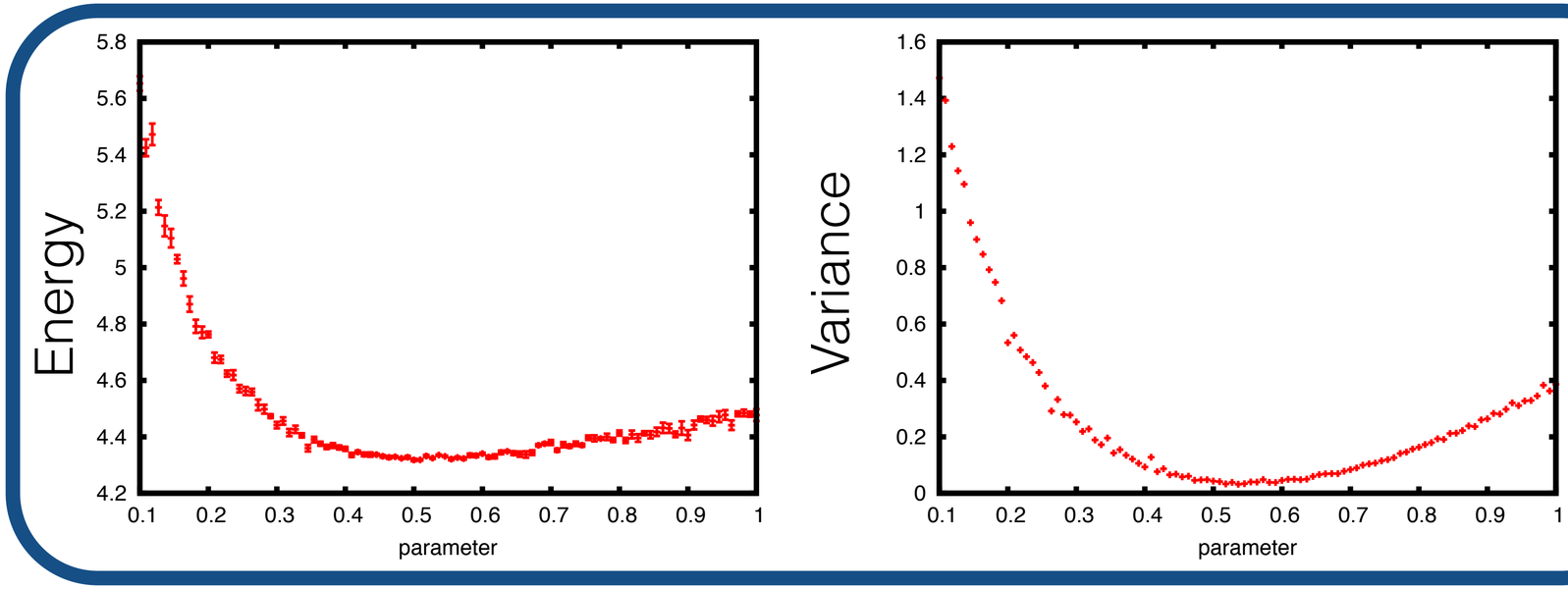
Generalization to any interaction strength: C/r_{12}, approximation $J(r_{12}) = \exp(Cr_{12}/(1 + \alpha r_{12}))$.

Results for two particles in 2D ho

C=1



C=3



Correlated wave function **Helium (spin singlet)**
(Replacement exercise available)

Very often used, simple generalization of Slater determinant:

$$\Psi(\mathbf{R}) = \det[\psi_i(\mathbf{r}_j)] \det[\psi_k(\mathbf{r}_l)] \prod J(r_{ij}) \ ,$$

where J is the Jastrow pair-correlation factor.

Has explicit dependence on the inter-electron distances, captures correlation.

Usually, both ψ and J have variational parameters.

Example: **Helium atom**

$$H = -\frac{1}{2}\sum_{i=1}^{2}(\nabla_i^2 + \frac{4}{r_i}) + \frac{1}{r_{12}} \ , \quad \psi = \exp(-\alpha r_1)\exp(-\alpha r_2)(1+\beta r_{12})$$

Trial wave function

Replacement homework (see Moodle)

Variational (Quantum) Monte Carlo

This week's problem is to calculate variationally the interacting total energy of a He atom (spin singlet, $S = 0$), using Variational Monte Carlo (VMC).
The related Fortran program for interacting bosons in harmonic confinement in 2D (`HO_2D.f90`), that was discussed during the lecture on Tuesday, should be useful for solving this homework.

1. Modify the example program so that it works in 3D (this is trivial), uses the correct nuclear potential instead of the harmonic one, and has a more appropriate trial wave function of the form

$$\Psi(r_1, r_2) = \exp(-\alpha r_1) \exp(-\alpha r_2) \exp(r_{12}/(1 + \beta r_{12})) \tag{1}$$

   Hint: Now you have 2 variational parameters instead of 1. It might be easiest from the point of view of Problem 2 to put both of these in a single array.

   Calculate the variational energy and variance of the local energy using parameter values $\alpha = 2$ and $\beta = 0.5$. (3 p)

2. Modify the VMC parameter optimization routine so that it can handle more parameters than just 1. Please also try switching the Jastrow pair-correlation factor to $(1 + \beta r_{12})$. How low can you go in energy and variance, what is the Jastrow and its parameter values then? What does the variance tell you about the trial wave function? (2 p)

   A side note: In principle you can experiment freely with the trial wave function to try to optimize it further as long as you conserve the symmetry/antisymmetry properties relevant for your system. However, in the case of the Coulomb interaction there is the problem that the potential energy diverges at close distances. The wave function (and thereby the kinetic energy) can be corrected to cancel this singularity by taking into account the so-called "Kato's cusp conditions". Both of the above Jastrow forms obey these. If you see instabilities / divergencies in your experiments you are probably violating them.

Helium atom (atomic units used)

$$\exp(-2r_1)\exp(-2r_2)$$

```
Energy is   -2.7501650455570168
 +/-   9.8006678941362658E-003
variance     1.1488288479043414
```

$$\exp(-\alpha r_1)\exp(-\alpha r_2)$$

```
Energy is   -2.8599094712349666
 +/-   5.2197236174658249E-003
variance    0.92130985411787947
```

Compare with the best fermion mean-field (Hartree-Fock) energy -2.862 a.u.

Taking the electron-electron coordinate to the wave function, captures “correlation” of electrons:

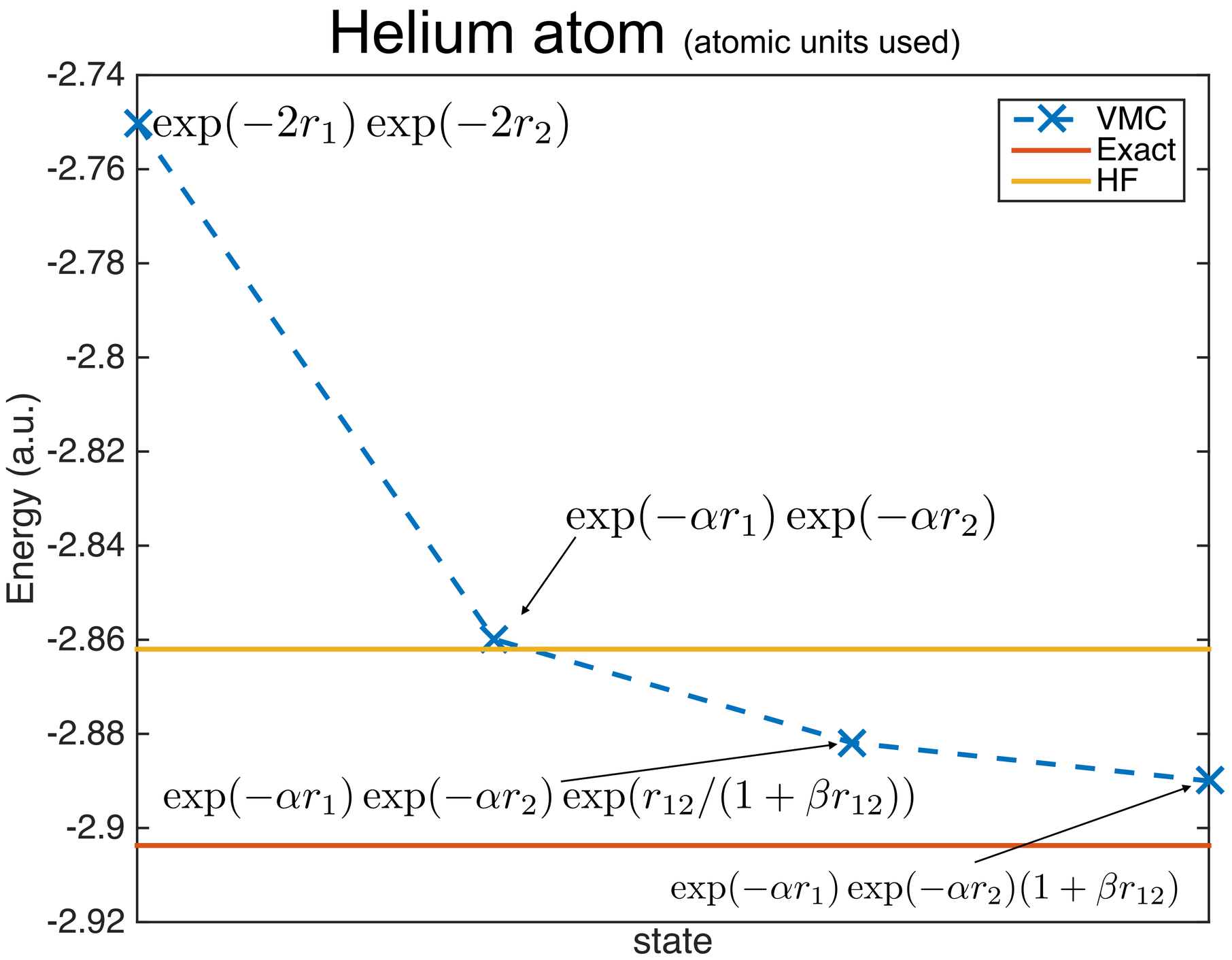
$$\exp(-\alpha r_1)\exp(-\alpha r_2)\exp(r_{12}/(1+\beta r_{12}))$$

```
Energy is   -2.8818722117420039
 +/-   4.7582387746590623E-003
variance    0.31314694883931438
```

$$\exp(-\alpha r_1)\exp(-\alpha r_2)(1+\beta r_{12})$$

```
Energy is   -2.8900060069843461
 +/-   2.8903137213841155E-003
variance    0.18910269919078004
```

“Exact” energy -2.90372 a.u.


Helium atom (atomic units used)
-2.74
-2.76
-2.78
-2.8
-2.82
-2.84
-2.86
-2.88
-2.9
-2.92
Energy (a.u.)
state
VMC
Exact
HF
$\exp(-2r_1)\exp(-2r_2)$
$\exp(-\alpha r_1)\exp(-\alpha r_2)$
$\exp(-\alpha r_1)\exp(-\alpha r_2)\exp(r_{12}/(1+\beta r_{12}))$
$\exp(-\alpha r_1)\exp(-\alpha r_2)(1+\beta r_{12})$

Beyond variational QMC

- Other popular techniques (see Gould-Tobochnik): Diffusion Monte Carlo, Path Integral Monte Carlo
- Main idea of Diffusion MC: The time-dependent Schrödinger equation looks bit like a diffusion equation in imaginary time

$$i\frac{\partial\Psi(\mathbf{R},t)}{\partial t} = -\frac{1}{2}\sum\nabla_i^2\Psi(\mathbf{R},t) + [V(\mathbf{R}) - E_T]\Psi(\mathbf{R},t)$$

- E_T is an arbitrary parameter that only shifts the zero of potential. We adjust it so that the distribution stays rather stationary, and the average of E_T then represents an eigenstate energy.
- For fermions, the wave function cannot be interpreted as probability density since in the general case it changes sign (the asymmetry property). Simplest cure: the fixed-node method that forbids moves that change the sign (we assume the nodal structure of a VMC wave function).
- Fermion system calculations usually start with VMC and DMC is the next step providing more accuracy.

Conclusions

- Quantum Monte Carlo is a powerful method for studying interacting quantum systems with many particles. Storing and sampling the wave function is straightforward.

- Inherently parallelizable — big computing clusters with thousands of cores can be applied easily