

Quantum Monte Carlo Methods for Abinitio Hamiltonians in Chemistry and Physics

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Outline

Subject 1: Basics

1. Quantum Monte Carlo in a nutshell.
2. Basics of Monte Carlo Methods

Subject 2: Variational Monte Carlo

1. Metropolis-Hastings algorithm
2. Forms of wave functions
3. Optimization of many-body wave functions

Subject 3: Projector Monte Carlo

1. Diffusion Monte Carlo
2. Full Configuration Interaction Quantum Monte Carlo
3. Auxiliary Field Quantum Monte Carlo / Determinantal Monte Carlo
4. Fermion Sign Problem

Solving the Many-Body Schrödinger Equation

Straightforward approach:

1. Expand the many-body wavefunction as a linear combination of (possibly nonorthogonal) basis states (determinants for Fermions).
2. Compute Hamiltonian and overlap matrices, H and S in this basis
3. Solve the generalized eigenvalue problem $Hc = ES c$

Problem:

The number of many-body states grows combinatorially in the number of single particle basis states and the number of particles, $\binom{N_{\text{orb}}}{N_{\uparrow}} \times \binom{N_{\text{orb}}}{N_{\downarrow}}$, e.g.

Half-filled 2D Hubbard model on 8×8 lattice: $\binom{64}{32}^2 = 3.3 \times 10^{36}$

Half-filled 2D Hubbard model on 16×16 lattice: $\binom{256}{128}^2 = 3.3 \times 10^{151}$

Molecules with 20 electrons in 200 orbitals: $\binom{200}{10}^2 = 5.0 \times 10^{32}$

(Partial) Solutions:

1. If only a small fraction, say 10^{10} of these states are important, then one can use smart methods for finding these states and diagonalizing.
2. Use Quantum Monte Carlo methods.

What is Quantum Monte Carlo?

Stochastic implementation of the power method for projecting out the dominant eigenvector of a matrix or integral kernel.

“Dominant state” means state with largest absolute eigenvalue.

If we repeatedly multiply an arbitrary vector, not orthogonal to the dominant state, by the matrix, we will eventually project out the dominant state.

Power method is an iterative method for eigenvalue problems (less efficient than Lanczos or Davidson). However, *stochastic* power method, QMC, is powerful.

QMC methods are used only when the number of states is so large ($> 10^{10}$) that it is not practical to store even a single vector in memory. Otherwise use exact diagonalization method, e.g., Lanczos or Davidson. At each MC generation, only a sample of the states are stored, and expectation values are accumulated.

QMC methods are used not only in a large discrete space but also in a continuously infinite space. Hence “matrix or integral kernel” above. In the interest of brevity I will use either discrete or continuous language (sums and matrices or integrals and integral kernels), but much of what is said will apply to both situations.

Zoo of Quantum Monte Carlo methods

There are a large number of QMC methods with a bewildering array of names, but just like a Chipotle wrap they are comprised of a few ingredients.

Chipotle wrap

white rice or brown rice
mild or medium or hot salsa
steak or carnitas or chicken or sofritas

QMC

zero temperature or finite temperature
linear projector or exponential projector
first quantized or second quantized
discrete time or continuous time
finite basis (site, Gaussian, planewave, ...) or infinite basis (real-space)
fixed-node or release-node
constrained-path or phaseless or free projection
finite path with Metropolis or open-ended walk with branching
pure estimator or mixed estimator or extrapolated estimator
single site or cluster or loop or worm updates

In these lectures we will see what all of the above mean (except the last line).

Definitions

Given a complete or incomplete basis: $\{|\phi_i\rangle\}$, either discrete or continuous

$$\text{Exact} \quad |\Psi_0\rangle = \sum_i e_i |\phi_i\rangle, \quad \text{where,} \quad e_i = \langle \phi_i | \Psi_0 \rangle$$

$$\text{Trial} \quad |\Psi_T\rangle = \sum_i t_i |\phi_i\rangle, \quad \text{where,} \quad t_i = \langle \phi_i | \Psi_T \rangle$$

$$\text{Guiding} \quad |\Psi_G\rangle = \sum_i g_i |\phi_i\rangle, \quad \text{where,} \quad g_i = \langle \phi_i | \Psi_G \rangle$$

(If basis incomplete then “exact” means “exact in that basis”.)

Ψ_T used to calculate variational and mixed estimators of operators \hat{A} , i.e., $\langle \Psi_T | \hat{A} | \Psi_T \rangle / \langle \Psi_T | \Psi_T \rangle$, $\langle \Psi_T | \hat{A} | \Psi_0 \rangle / \langle \Psi_T | \Psi_0 \rangle$

Ψ_G used to alter the probability density sampled, i.e., Ψ_G^2 in VMC, $\Psi_G \Psi_0$ in PMC.

Ψ_G must be such that $g_i \neq 0$ if $e_i \neq 0$. If Ψ_T also satisfies this condition then Ψ_G can be chosen to be Ψ_T . Reasons to have $\Psi_G \neq \Psi_T$ are: a) rapid evaluation of “local energy”, b) have finite-variance estimators. To simplify expressions, we sometimes use $\Psi_G = \Psi_T$ or $\Psi_G = 1$ in what follows.

Variational MC

$$\begin{aligned}
 E_V &= \frac{\langle \Psi_T | \hat{H} | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle} = \frac{\sum_{ij}^{N_{st}} \langle \Psi_T | \phi_i \rangle \langle \phi_i | \hat{H} | \phi_j \rangle \langle \phi_j | \Psi_T \rangle}{\sum_i^{N_{st}} \langle \Psi_T | \phi_k \rangle \langle \phi_k | \Psi_T \rangle} \\
 &= \frac{\sum_{ij}^{N_{st}} t_i H_{ij} t_j}{\sum_k^{N_{st}} t_k^2} = \sum_i^{N_{st}} \frac{t_i^2}{\sum_k^{N_{st}} t_k^2} \frac{\sum_j^{N_{st}} H_{ij} t_j}{t_i} \\
 &= \sum_i^{N_{st}} \frac{t_i^2}{\sum_k^{N_{st}} t_k^2} E_L(i) = \frac{\left[\sum_i^{N_{MC}} E_L(i) \right]_{\Psi_T^2}}{N_{MC}} \xrightarrow{\Psi_G \neq \Psi_T} \frac{\left[\sum_i^{N_{MC}} \left(\frac{t_i}{g_i} \right)^2 E_L(i) \right]_{\Psi_G^2}}{\left[\sum_k^{N_{MC}} \left(\frac{t_k}{g_k} \right)^2 \right]_{\Psi_G^2}}
 \end{aligned}$$

Sample probability density function $\frac{g_i^2}{\sum_k^{N_{st}} g_k^2}$ using Metropolis-Hastings, if Ψ_G complicated.

Value depends only on Ψ_T . Statistical error depend on Ψ_T and Ψ_G .

Energy bias and statistical error vanish as $\Psi_T \rightarrow \Psi_0$.

For fixed Ψ_T , $\Psi_G = \Psi_T$ does not minimize statistical fluctuations!

In fact $\Psi_G \neq \Psi_T$ needed when optim. to get finite variance.

$\Psi_G = \Psi_T$ allows simple unbiased estimator. Ratio of expec. val. \neq expec. val. of ratios.

Projector MC

Pure and Mixed estimators for energy are equal: $E_0 = \frac{\langle \Psi_0 | \hat{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} = \frac{\langle \Psi_0 | \hat{H} | \Psi_T \rangle}{\langle \Psi_0 | \Psi_T \rangle}$

Projector: $|\Psi_0\rangle = \hat{P}(\infty) |\Psi_T\rangle = \lim_{n \rightarrow \infty} \hat{P}^n(\tau) |\Psi_T\rangle$

$$\begin{aligned}
 E_0 &= \frac{\langle \Psi_0 | \hat{H} | \Psi_T \rangle}{\langle \Psi_0 | \Psi_T \rangle} = \frac{\sum_{ij}^{N_{st}} \langle \Psi_0 | \phi_i \rangle \langle \phi_i | \hat{H} | \phi_j \rangle \langle \phi_j | \Psi_T \rangle}{\sum_k^{N_{st}} \langle \Psi_0 | \phi_k \rangle \langle \phi_k | \Psi_T \rangle} \\
 &= \frac{\sum_{ij}^{N_{st}} e_i H_{ij} t_j}{\sum_k^{N_{st}} e_k t_k} = \sum_i \frac{e_i t_i}{\sum_k^{N_{st}} e_k t_k} \frac{\sum_j^{N_{st}} H_{ij} t_j}{t_i} \\
 &= \sum_i \frac{e_i t_i}{\sum_k^{N_{st}} e_k t_k} E_L(i) = \frac{\left[\sum_i^{N_{MC}} E_L(i) \right]_{\Psi_T \Psi_0}}{N_{MC}} \xrightarrow{\Psi_G \neq \Psi_T} \frac{\left[\sum_i^{N_{MC}} \left(\frac{t_i}{g_i} \right) E_L(i) \right]_{\Psi_G \Psi_0}}{\left[\sum_k^{N_{MC}} \left(\frac{t_k}{g_k} \right) \right]_{\Psi_G \Psi_0}}
 \end{aligned}$$

Sample $e_i g_i / \sum_k^{N_{st}} e_k g_k$ using *importance-sampled* projector.

For exact PMC, value indep. of Ψ_T , Ψ_G , statistical error depends on Ψ_T , Ψ_G .

(For FN-PMC, value depends on Ψ_G , statistical error on Ψ_T , Ψ_G .)

(For FN-DMC, value depends on nodes of Ψ_G , statistical error on Ψ_T , Ψ_G .)

Statistical error vanishes as $\Psi_T \rightarrow \Psi_0$.

For fixed Ψ_T , $\Psi_G = \Psi_T$ does not minimize statistical fluctuations!

Variational and Projector MC

$$E_V = \frac{\left[\sum_i^{N_{\text{MC}}} \left(\frac{t_i}{g_i} \right)^2 E_L(i) \right]_{\Psi_G^2}}{\left[\sum_k^{N_{\text{MC}}} \left(\frac{t_k}{g_k} \right)^2 \right]_{\Psi_G^2}} \quad (\text{Value depends on } \Psi_T, \text{ error } \Psi_T, \Psi_G)$$

$$E_0 = \frac{\left[\sum_i^{N_{\text{MC}}} \left(\frac{t_i}{g_i} \right) E_L(i) \right]_{\Psi_G \Psi_0}}{\left[\sum_k^{N_{\text{MC}}} \left(\frac{t_k}{g_k} \right) \right]_{\Psi_G \Psi_0}} \quad (\text{Value exact}^\dagger. \text{ Error depends on } \Psi_T, \Psi_G.)$$

$$E_L(i) = \frac{\sum_j^{N_{\text{st}}} H_{ij} t_j}{t_i}$$

In both VMC and PMC weighted average of the *configuration value of \hat{H}* aka *local energy, $E_L(i)$* , but from points sampled from different distributions.

This is practical for systems that are large enough to be interesting if

1. $t_i = \langle \phi_i | \Psi_T \rangle$, $g_i = \langle \phi_i | \Psi_G \rangle$ can be evaluated in polynomial time, say N^3
2. the sum in $E_L(i)$ can be done quickly, i.e., \hat{H} is sparse (if space discrete) or semi-diagonal (if space continuous).

[†] In practice, usually necessary to make approximation (e.g. FN) and value depends on Ψ_G .

Variational Monte Carlo in Real Space

W. L. McMillan, Phys. Rev. **138**, A442 (1965)

Real space $\implies |\phi_i\rangle = |\mathbf{R}\rangle$. Monte Carlo is used to perform the many-dimensional integrals needed to calculate quantum mechanical expectation values. e.g.

$$\begin{aligned} E_T &= \frac{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \mathcal{H} \psi_T(\mathbf{R})}{\int d\mathbf{R} \psi_T^2(\mathbf{R})} \\ &= \int d\mathbf{R} \frac{\psi_T^2(\mathbf{R})}{\int d\mathbf{R} \psi_T^2(\mathbf{R})} \frac{\mathcal{H}\psi_T(\mathbf{R})}{\psi_T(\mathbf{R})} \\ &= \frac{1}{N} \sum_i \frac{\mathcal{H}\Psi_T(\mathbf{R}_i)}{\Psi_T(\mathbf{R}_i)} = \frac{1}{N} \sum_i E_L(\mathbf{R}_i) \end{aligned}$$

Energy is obtained as an arithmetic sum of the *local energies* $E_L(\mathbf{R}_i)$ evaluated for configurations sampled from $\psi_T^2(\mathbf{R})$ using a generalization of the Metropolis method. If ψ_T is an eigenfunction, the $E_L(\mathbf{R}_i)$ do not fluctuate. Accuracy of VMC depends crucially on the quality of $\psi_T(\mathbf{R})$.

Diffusion MC does better by projecting onto ground state.

Rest of this lecture

Now that you know the essence of quantum Monte Carlo methods, for the rest of this lecture we will discuss basic concepts that underlie both classical and quantum Monte Carlo methods, e.g., the central limit theorem, techniques for sampling various distributions, importance sampling for reducing statistical error, calculation of unbiased estimators, ...

Then in the rest of the lectures we will continue our study of quantum Monte Carlo methods.

When to use Monte Carlo Methods

Monte Carlo methods: A class of computational algorithms that rely on repeated random sampling to compute results.

A few broad areas of applications are:

1. physics
2. chemistry
3. engineering
4. finance and risk analysis

When are MC methods likely to be the methods of choice?

1. When the problem is many-dimensional and approximations that factor the problem into products of lower dimensional problems are inaccurate.
2. A less important reason is that if one has a complicated geometry, a MC algorithm may be simpler than other choices.

Obvious drawback of MC methods: There is a statistical error.

Frequently there is a tradeoff between statistical error and systematic error and one needs to find the best compromise.

MC Simulations versus MC calculations

One can distinguish between two kinds of algorithms:

1. The system being studied is stochastic and the stochasticity of the algorithm mimics the stochasticity of the actual system. e.g. study of neutron transport and decay in nuclear reactor by following the trajectories of a large number of neutrons. Such problems are suitable for MC algorithms in a very obvious way.
2. Much more interesting are applications where the system being studied is not stochastic, but nevertheless a stochastic algorithm is the most efficient, or the most accurate, or the only feasible method for studying the system. e.g. the solution of a PDE in a large number of variables, e.g., the solution of the Schrödinger equation for an N -electron system, with say $N = 100$ or 1000 . (Note: The fact that the wavefunction has a probabilistic interpretation has *nothing* to do with the stochasticity of the algorithm. The wavefunction itself is perfectly deterministic.)

I prefer to use the terminology that the former are **MC simulations** whereas the latter are **MC calculations** but not everyone abides by that terminology.

Early Recorded History of Monte Carlo

- 1777 **Comte de Buffon:** If a needle of length L is thrown at random onto a plane ruled with straight lines a distance d ($d > L$) apart, then the probability P of the needle intersecting one of those lines is $P = \frac{2L}{\pi d}$.
- Laplace:** This could be used to compute π (inefficiently).
- 1930s First significant scientific application of MC: **Enrico Fermi** used it for neutron transport in fissile material.
- Segre:** "Fermi took great delight in astonishing his Roman colleagues with his "too-good-to-believe" predictions of experimental results."
- 1940s Monte Carlo named by **Nicholas Metropolis and Stanislaw Ulam**
- 1953 Algorithm for sampling **any** probability density
- Metropolis, Rosenbluth, Rosenbluth, Teller and Teller** (generalized by **Hastings** in 1970)
- 1962,1974 First PMC calculations, **Kalos, and, Kalos, Levesque, Verlet.**
- 1965 First VMC calculations (of liquid He), **Bill McMillan.**

Compte de Buffon

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Here he is:

Among other things, he wrote a 36 volume set of books on the Natural History of the Earth!

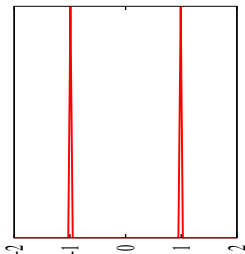
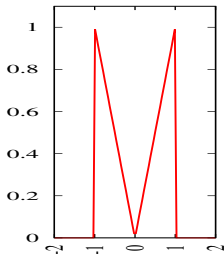
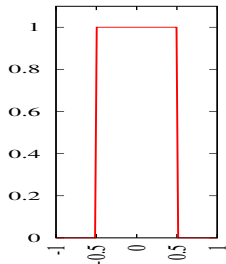


Central Limit Theorem

de Moivre (1733), Laplace (1812), Lyapunov (1901), Pólya (1920)

Let $X_1, X_2, X_3, \dots, X_N$ be a sequence of N independent random variables sampled from a probability density function with a finite expectation value, μ , and variance σ^2 . The central limit theorem states that as the sample size N increases, the probability density of the sample average, \bar{X} , of these random variables approaches the normal distribution,

$\sqrt{\frac{N}{2\pi\sigma^2}} e^{-(x-\mu)^2/(2\sigma^2/N)}$, with mean μ , and variance σ^2/N , irrespective of the original probability density function, e.g.:



The rate at which they converge will however depend on the original PDF.

(Weak) Law of Large Numbers

Cardano, Bernouli, Borel, Cantelli, Kolmogorov, Khinchin

Let $X_1, X_2, X_3, \dots, X_N$ be a sequence of N independent random variables sampled from a probability density function with a finite expectation value, μ , but not necessarily a finite variance σ^2 . Then for any $\epsilon > 0$,

$$\lim_{N \rightarrow \infty} P(|\bar{X} - \mu| \geq \epsilon) = 0$$

However, the rate at which it converges may be very slow.
So, employ distributions with a finite variance whenever possible.

Lorentzian

Does the **Central Limit Theorem** or the **Law of Large Numbers** apply to a Lorentzian (also known as Cauchy) probability density function

$$L(x) = \frac{1}{\pi} \frac{1}{1+x^2}?$$

Lorentzian

A Lorentzian (also known as Cauchy) probability density function

$$L(x) = \frac{1}{\pi} \frac{1}{1+x^2}$$

not only violates the conditions for the [Central Limit Theorem](#) but also the conditions for the [Law of Large Numbers](#), since not only the variance but even the mean is undefined.

$$\begin{aligned} \int_{-\infty}^{\infty} xL(x)dx &= \left(\int_{-\infty}^a + \int_a^{\infty} \right) xL(x)dx \\ &= -\infty + \infty \end{aligned}$$

Averages over a Lorentzian have the same spread of values as the original values!

So, although the Lorentzian looks much “nicer” than the other 3 functions we showed, it is a problem!

Chebyshev Inequality

The Central Limit Theorem by itself does not tell you how quickly the averages converge to a Gaussian distribution.

For an arbitrary distribution with finite mean μ and finite variance σ^2 , we have much weaker bounds given by Chebyshev's inequality:

The probability of a variable lying between $\mu - n\sigma$ and $\mu + n\sigma$ is $> 1 - 1/n^2$, as compared to $\text{erf}(n/\sqrt{2})$ for a Gaussian.

Prob. of being within 1σ of μ is $\geq 0\%$ versus 68.3% for Gaussian

Prob. of being within 2σ of μ is $\geq 75\%$ versus 95.4% for Gaussian

Prob. of being within 3σ of μ is $\geq 89\%$ versus 99.7% for Gaussian

Prob. of being within 4σ of μ is $\geq 94\%$ versus 99.994% for Gaussian

The worst case occurs for a distribution with probability $1 - 1/n^2$ at μ and probability $1/2n^2$ at $\mu - n\sigma$ and $\mu + n\sigma$.

What if the population variance $\sigma^2 = \infty$ but we do not know that beforehand? The computed sample variance will ofcourse always be finite. The practical signature of an infinite variance estimator is that the estimated σ increases with sample size, N and tends to have upward jumps. So the estimated error of the sample mean, $\sigma_N = \sigma/\sqrt{N}$, goes down more slowly than $\frac{1}{\sqrt{N}}$, or even does not go down at all.

Monte Carlo versus Deterministic Integration methods

Deterministic Integration Methods:

Integration Error, ϵ , using N_{int} integration points:

1-dim Simpson rule: $\epsilon \leq cN_{\text{int}}^{-4}$, (provided derivatives up to 4th exist)

d -dim Simpson rule: $\epsilon \leq cN_{\text{int}}^{-4/d}$, (provided derivatives up to 4th exist)

This argument is correct for functions that are approximately separable.

Monte Carlo:

$\epsilon \sim \sigma(T_{\text{corr}}/N_{\text{int}})^{1/2}$, **independent of dimension!**, according to the **central limit theorem** since width of gaussian decreases as $(T_{\text{corr}}/N_{\text{int}})^{1/2}$ provided that the variance of the integrand is finite. (T_{corr} is the autocorrelation time.)

Very roughly, Monte Carlo becomes advantageous for $d > 8$.

For $d = 30$, even 2 grid points per dimensions gives $N_{\text{int}} \approx 10^9$, so deterministic integration not possible.

For a many-body wavefunction $d = 3N_{\text{elec}}$ and can be a few thousand!

Scaling with number of electrons

Simpson's rule integration

$$\epsilon \leq \frac{C}{N_{\text{int}}^{4/d}} = \frac{C}{N_{\text{int}}^{4/3N_{\text{elec}}}}$$
$$N_{\text{int}} \leq \left(\frac{C}{\epsilon}\right)^{\frac{3N_{\text{elec}}}{4}} \quad \text{exponential in } N_{\text{elec}}$$

Monte Carlo integration

$$\epsilon = \sigma \sqrt{\frac{N_{\text{elec}}}{N_{\text{MC}}}}$$
$$N_{\text{MC}} = \left(\frac{\sigma}{\epsilon}\right)^2 N_{\text{elec}} \quad \text{linear in } N_{\text{elec}}$$

(For both methods, computational cost is higher than this since the cost of evaluating the wavefunction increases with N_{elec} , e.g., as N_{elec}^3 , (better if one uses “linear scaling”; worse if one increases N_{det} with N_{elec} .)

Monte Carlo Integration

$$I = \int_V f(x) dx = V \bar{f} \pm V \sqrt{\frac{\overline{f^2} - \bar{f}^2}{N-1}}$$

where $\bar{f} = \frac{1}{N} \sum_i^N f(x_i)$, $\overline{f^2} = \frac{1}{N} \sum_i^N f^2(x_i)$

and the points x_i are sampled uniformly in V . Many points may contribute very little.

Monte Carlo Integration

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and the points x_i are sampled uniformly in V . Many points may contribute very little.

Importance sampling

$$I = \int_V g(x) \frac{f(x)}{g(x)} dx = \overline{\left(\frac{f}{g}\right)} \pm \sqrt{\frac{\overline{\left(\frac{f}{g}\right)^2} - \left(\overline{\frac{f}{g}}\right)^2}{N-1}}$$

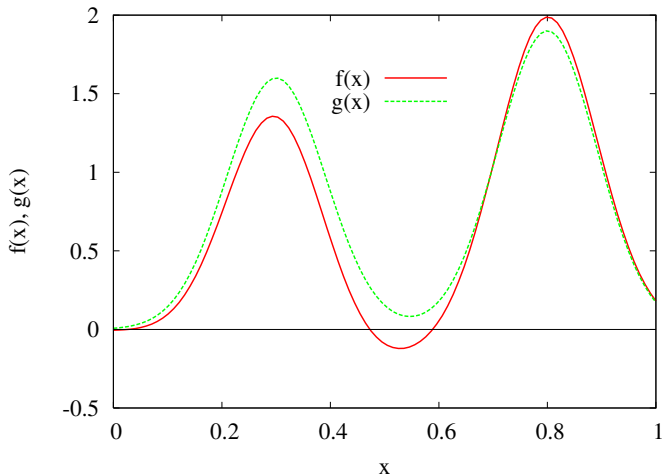
where the **probability density function** $g(x) \geq 0$ and $\int_V g(x) dx = 1$.

If $g(x) = 1/V$ in V then we recover original fluctuations but if $g(x)$ mimics $f(x)$ then the fluctuations are much reduced. Optimal g is $|f|$. Need: a) $g(x) \geq 0$, b) know integral of $g(x)$, and, c) be able to sample it.

Importance sampling can turn an ∞ -variance estimator into a finite variance one!

Illustration of Importance Sampling

$f(x)$ is the function to be integrated. $g(x)$ is a function that is “similar” to $f(x)$ and has the required properties: a) $g(x) \geq 0$, b) $\int dx g(x) = 1$, and, c) we know how to sample it. $\int f(x)dx$ can be evaluated efficiently by sampling $g(x)$ and averaging $f(x)/g(x)$.

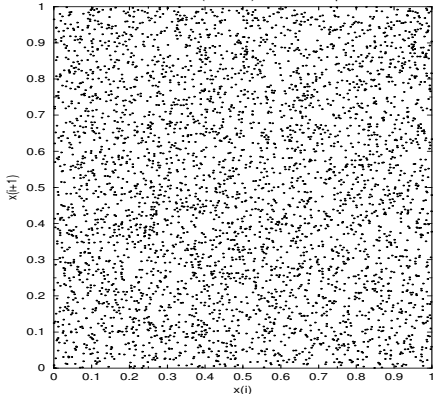


Pseudo-random vs quasi-random numbers

Terrible misnomers!

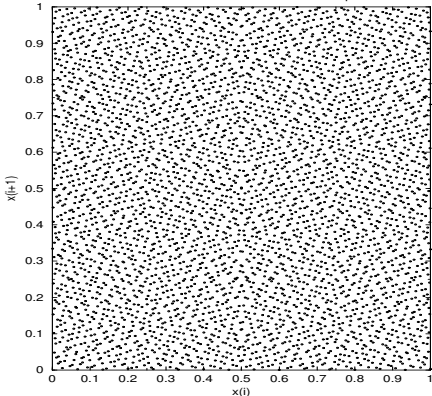
(Pseudo) Random Sequence

4096 Points of (Pseudo) Random Sequence



Quasi-Random Sobol Sequence

4096 Points of Quasi-Random Sobol Sequence



Reason why uniform grid is inefficient: Projection of $N = n^d$ points in d dimensions onto a line maps n^{d-1} points onto a single point.

Reason why quasi-MC is more efficient than pseudo-MC in intermediate # of dimensions (e.g. finance applications): Quasi-MC avoids clusters and voids.

Negatives for quasi-MC: Difficult to combine with importance sampling (needed for spiky functions), cannot choose # of MC points freely.

Sampling of arbitrary probability density functions

Infinite-variance estimators can be replaced by finite-variance estimators by sampling the MC points from an appropriate probability density functions.

Techniques for sampling arbitrary probability density functions employ standard random numbers generators that sample a uniform distribution in $[0, 1]$. We study 3 techniques for sampling nonuniform distributions:

1. transformation method
2. rejection method
3. Metropolis-Hastings method

but first we say a few words about random number generators.

Random Number Generators

Conventional random number generators generate random numbers uniformly distributed on $[0,1)$.

Of course no computer generated sequence of random numbers is truly random. For one, the random numbers must repeat after a finite (though hopefully very large) period. Also, if N bits are used to represent the random numbers, then the number of different numbers generated can be no larger than 2^N .

Note however, that the period can be (and typically is for the better generators) much larger than 2^N .

Many different algorithms exist for generating random numbers, e.g., linear congruential generators (with or without an additive constant), linear feedback shift register, lagged Fibonacci generator, XORshift algorithm etc. They are typically subjected to a battery of statistical tests, e.g., the [Diehard](#) tests of Marsaglia. Of course no random number generator can pass all the tests that one can invent, but hopefully the random number generator used does not have correlations that could significantly impact the system being studied.

Random Number Generators

For many MC calculations it is the short-ranged correlations that matter most, but one has to think for each application what is important. For example, if one were studying an Ising model with a power of two number of spins, it would be problematic to have random number generator that generated numbers with bits that repeat at an interval of 2^N .

In the old days, there were quite a few calculations that produced inaccurate results due to bad random number generators. For example, the standard generators that came with UNIX and with C were badly flawed. In the 1980s a special purpose computer was built at Santa Barbara to study the 3-D Ising model. However, at first it failed to reproduce the known exact results for the 2-D Ising model and that failure was traced back to a faulty random number generator. Fortunately, these days the standard random number generators are much more reliable.

Sampling random variables from nonuniform probability density functions

We say x is sampled from $f(x)$ if for any a and b in the domain,

$$\text{Prob}[a \leq x \leq b] = \int_a^b dx' f(x')$$

- 1) Transformation method (For many simple functions)
- 2) Rejection method (For more complicated functions)
- 3) Metropolis-Hastings method (For any function)

1) Transformation method: Perform a transformation $x(\xi)$ on a uniform deviate ξ , to get x sampled from desired probability density $f(x)$.

$$|\text{Prob}(\xi)d\xi| = |\text{Prob}(x)dx| \quad \text{conservation of probability}$$

If we have sampled ξ from a uniform density ($\text{Prob}(\xi) = 1$) and we wish x to be sampled from the desired density, $f(x)$, then setting $\text{Prob}(x) = f(x)$,

$$\left| \frac{d\xi}{dx} \right| = f(x)$$

Solve for $\xi(x)$ and invert to get $x(\xi)$, i.e., invert the cumulative distribution.

Examples of Transformation Method

Example 1: $f(x) = ae^{-ax}$, $x \in [0, \infty)$

$$\left| \frac{d\xi}{dx} \right| = ae^{-ax}, \quad \text{or,} \quad \xi = e^{-ax}, \quad \text{i.e.,} \quad \boxed{x = \frac{-\ln(\xi)}{a}}$$

Examples of Transformation Method

Example 1: $f(x) = ae^{-ax}$, $x \in [0, \infty)$

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Example 2: $f(x) = \frac{x^{-1/2}}{2}$, $x \in [0, 1]$

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Note that in this case we are sampling a probability density that is infinite at 0, but that is OK!

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Note that in this case we are sampling a probability density that is infinite at 0, but that is OK!

Example 3: $f(x) = xe^{-x^2/2}$, $x \in [0, \infty)$

$$\left| \frac{d\xi}{dx} \right| = xe^{-x^2/2}, \text{ or, } \xi = e^{-x^2/2}, \text{ i.e., } \boxed{x = \sqrt{-2\ln(\xi)}}$$

Examples of Transformation Method

Example 4a: $f(x) = \frac{e^{-x^2/2}}{\sqrt{2\pi}}$, $x \in (-\infty, \infty)$ (using Box-Müller method)

$$\frac{1}{2\pi} e^{-(\frac{x_1^2}{2} + \frac{x_2^2}{2})} dx_1 dx_2 = \left(r e^{-\frac{r^2}{2}} dr \right) \left(\frac{d\phi}{2\pi} \right)$$

$$r = \sqrt{-2 \log(\xi_1)},$$

$$\phi = 2\pi\xi_2$$

$$x_1 = \sqrt{-2 \log(\xi_1)} \cos(2\pi\xi_2),$$

$$x_2 = \sqrt{-2 \log(\xi_1)} \sin(2\pi\xi_2)$$

(x_1 and x_2 are uncorrelated)

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(x_1 and x_2 are uncorrelated)

Example 4b: $f(x) \approx \frac{e^{-x^2/2}}{\sqrt{2\pi}}$, $x \in (-\infty, \infty)$ (using central-limit theorem)

$\xi - 0.5$ is in $[-1/2, 1/2]$. Since σ^2 for uniform distribution about 0 is

$$\int_{-1/2}^{1/2} dx x^2 = \frac{1}{12}$$

$$x = \lim_{N \rightarrow \infty} \sqrt{\frac{12}{N}} \left(\sum_{i=1}^N \xi_i - \frac{N}{2} \right) \approx \sum_{i=1}^{12} \xi_i - 6$$

(avoids log, sqrt, cos, sin, but, misses tiny tails beyond ± 6)

Rejection Method

We wish to sample $f(x)$.

Find a function $g(x)$ that can be sampled by another method (say transformation) and that preferably mimics the behaviour of $f(x)$.

Let $C \geq \max(f(x)/g(x))$.

Then $f(x)$ is sampled by sampling $g(x)$ and keep the sampled points with probability

$$P = \frac{f(x)}{Cg(x)}$$

The efficiency of the method is the fraction of the sampled points that are kept.

$$\begin{aligned} \text{Eff} &= \int dx \frac{f(x)}{Cg(x)} g(x) \\ &= \frac{1}{C} \end{aligned}$$

Drawback: It is often hard to know C and a “safe” upperbound choice for C may lead to low efficiency. An alternative is to associate weights with the sampled points.

Sampling from Discrete Distributions

Suppose we need to repeatedly sample from N discrete events with probabilities p_1, p_2, \dots, p_N , where N is large.

What is the best possible scaling of the time per sample?

Is it $\mathcal{O}(N)$, $\mathcal{O}(\log_2(N))$, $\mathcal{O}(1)$?

Sampling from Discrete Distributions

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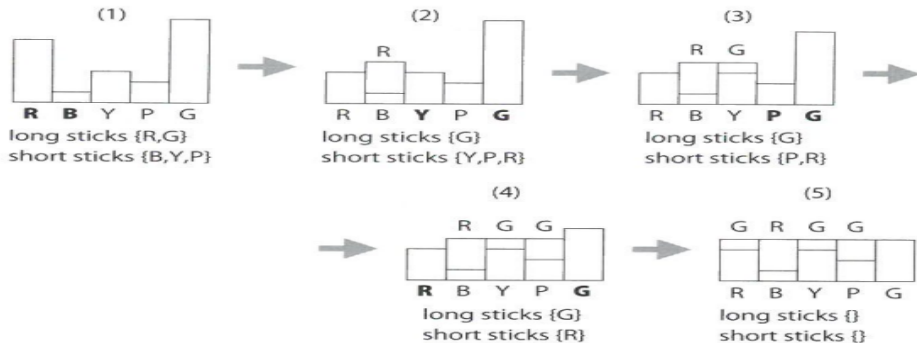
Is it $\mathcal{O}(N)$, $\mathcal{O}(\log_2(N))$, $\mathcal{O}(1)$?

Straightforward $\mathcal{O}(\log_2(N))$ method with binary search:

1. Before starting sampling, construct array of cumulative probabilities.
2. Draw a random number, ξ , in $[0, 1]$.
3. Do a binary search to find the interval it falls in.

Can we do it in $\mathcal{O}(1)$?

Sampling from Discrete Distributions: $O(1)$ Alias Method



1. Before starting sampling, construct an integer array, $\{A_i\}$, that contains the aliases and a real array, $\{p_i\}$ that contains the probabilities of staying at i .
2. Draw a random number in $[0, 1]$.
3. Go to the $i = \lceil N\xi \rceil$ bin.
4. With probability p_i sample i and with probability $(1 - p_i)$ sample A_i .

Figure taken from book by Gubernatis, Kawashima and Werner

Importance Sampling for computing integrals efficiently

Now that we know how to sample simple probability density functions, we study how to use *importance sampling* to compute integrals more efficiently.

Example of Importance Sampling to Calculate Integrals More Efficiently

Suppose we wish to compute

$$\int_0^1 dx f(x) = \int_0^1 dx \frac{1}{x^p + x} \left(= \frac{\log\left(\frac{x+x^p}{x^p}\right)}{1-p} \right) \Bigg|_0^1 = \frac{\log(2)}{1-p}, \quad \text{but pretend not known}$$

Note that

$$\int_0^1 dx (f(x))^2 = \infty, \quad (\text{for } p \geq 0.5)$$

so if we estimate the integral by sampling points uniformly in $[0, 1]$ then this would be an **infinite variance estimator** and the error of the estimate will go down more slowly than $N^{-1/2}$. However, we can instead sample points from the density

$$g(x) = \frac{1-p}{x^p}$$

Now the variance of $f(x)/g(x)$ is finite and the error decreases as $N^{-1/2}$, and, with a small prefactor. **(Still would not use this in 1D.)**

Homework Problem 1

Compute

$$I = \int_0^1 dx f(x) = \int_0^1 dx \frac{1}{x^p + x} \quad (= \frac{\log(2)}{1-p}, \text{ but pretend not known}) \approx \frac{1}{N_{\text{MC}}} \sum_{k=1}^{N_{\text{MC}}} \frac{1}{\xi_k^p + \xi_k}$$

with/without importance sampling, using for the importance sampling function

$$g(x) = \frac{(1-p)}{x^p}$$

To sample $g(x)$: $\left| \frac{d\xi}{dx} \right| = (1-p)x^{-p}$, i.e., $\xi = x^{1-p}$, i.e., $x = \xi^{\frac{1}{1-p}}$

$$\begin{aligned} \int_0^1 dx f(x) &= \int_0^1 dx g(x) \frac{f(x)}{g(x)} = \int_0^1 dx \frac{1-p}{x^p} \frac{1}{(1-p)(1+x^{1-p})} \\ &\approx \frac{1}{N_{\text{MC}}(1-p)} \sum_{k=1}^{N_{\text{MC}}} \frac{1}{(1+x_k^{1-p})} = \frac{1}{N_{\text{MC}}(1-p)} \sum_{k=1}^{N_{\text{MC}}} \frac{1}{(1+\xi_k)} \end{aligned}$$

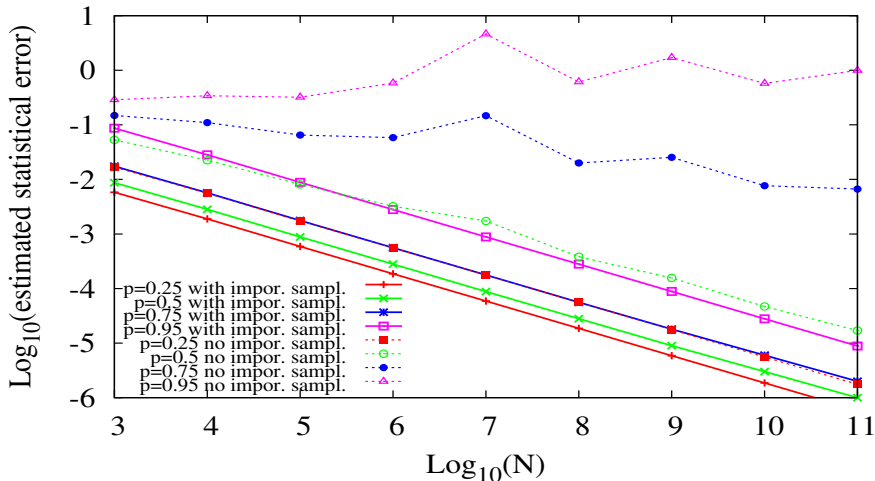
Do this for $p = 0.25, 0.5, 0.75, 0.95$ and $N_{\text{MC}} = 10^3, 10^4, 10^5, 10^6, 10^7, 10^8, 10^9$.

Plot 2 graphs, each having 8 curves (4 values of p , and, with/without importance sampling):

1. Log of estimated 1-standard deviation statistical error versus $\log(N_{\text{MC}})$.
2. Actual error in I , with estimated 1-std. dev. statistical error as an error bar versus $\log(N_{\text{MC}})$.

Homework Solution 1a

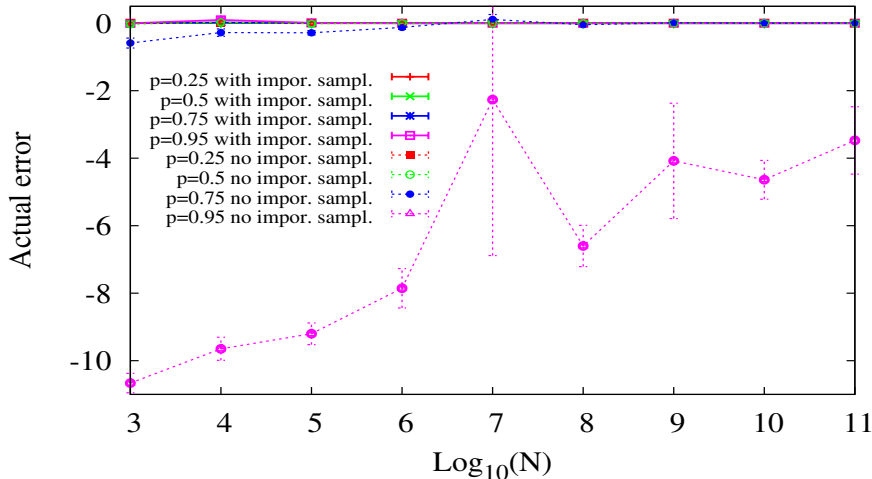
MC integral of $1/(x^p+x)$ with and without importance sampling



Statistical errors $\sim N_{MC}^{-1/2}$ for all p with importance sampling but only for $p = 0.25$ without importance sampling. For $p = 1$ even the integral is infinite. For $p = 0.95$ no sign of convergence. Theorem about asymptotic convergence of little practical utility.

Homework Solution 1b

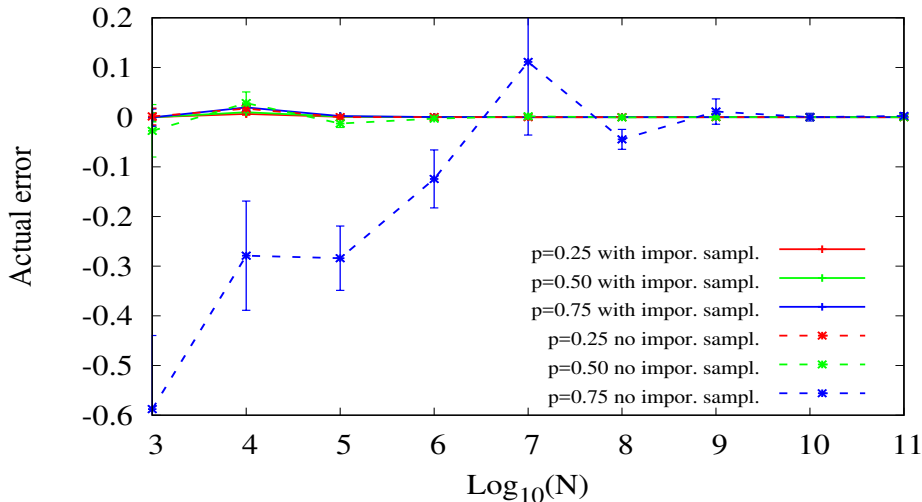
MC integral of $1/(x^p+x)$ with and without importance sampling



For $p = 0.95$ all of the errors are negative. Occasional large positive errors will bring mean to correct value. Actual errors may be MANY standard deviations. For infinite variance highly skewed variables the averages with the larger actual errors tend to have the smaller estimated errors! So, weighting estimates by inverse variances is bad!!

Homework Solution 1b (expanded scale)

MC integral of $1/(x^p+x)$ with and without importance sampling



Beware of infinite-variance estimators, particularly if the distribution of estimates is highly skewed!

Unbiased Estimators

Population mean: $\langle f \rangle$

Sample (of size N) mean: \bar{f}

$\tilde{F}(\bar{f})$ is an unbiased estimator if $\langle \tilde{F}(\bar{f}) \rangle = F(\langle f \rangle)$

or more generally

$\tilde{F}(\bar{f}_1, \bar{f}_2, \dots)$ is an unbiased estimator if $\langle \tilde{F}(\bar{f}_1, \bar{f}_2, \dots) \rangle = F(\langle f_1 \rangle, \langle f_2 \rangle, \dots)$

1) Is $\langle \bar{f} - \bar{g} \rangle = \langle f \rangle - \langle g \rangle$?

2) Is $\langle \bar{f}\bar{g} \rangle = \langle f \rangle \langle g \rangle$?

3) Is $\langle \bar{f}/\bar{g} \rangle = \langle f \rangle / \langle g \rangle$?

4) Is $\langle \bar{f}^2 - \bar{f}^2 \rangle = \langle f^2 \rangle - \langle f \rangle^2$?

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1) Is $\langle \bar{f} - \bar{g} \rangle = \langle f \rangle - \langle g \rangle$? **yes**

2) Is $\langle \bar{f}\bar{g} \rangle = \langle f \rangle \langle g \rangle$? **no**

3) Is $\langle \bar{f}/\bar{g} \rangle = \langle f \rangle / \langle g \rangle$? **no**

4) Is $\langle \bar{f}^2 - \bar{f}^2 \rangle = \langle f^2 \rangle - \langle f \rangle^2$? **no**. Correct: $\frac{N}{N-1} \langle \bar{f}^2 - \bar{f}^2 \rangle = \langle f^2 \rangle - \langle f \rangle^2$

Estimating Unbiased Variance from Uncorrelated Samples

Let $\langle f(x) \rangle$ denote the population mean and $\bar{f}(x)$ denote the sample mean.

Then $\overline{f^2} - (\bar{f})^2 =$

$$\left\langle \frac{\sum_i f^2(x_i)}{N} - \left[\frac{\sum_i f(x_i)}{N} \right]^2 \right\rangle = \langle f^2 \rangle - \left\langle \frac{\sum_i f^2(x_i) + \sum_{i,j \neq i} \sum_j f(x_i)f(x_j)}{N^2} \right\rangle$$

Since $f(x_i)$ and $f(x_j)$ are independent

$$RHS = \left(1 - \frac{1}{N}\right) \langle f^2 \rangle - \frac{N(N-1)}{N^2} \langle f \rangle^2 = \frac{N-1}{N} (\langle f^2 \rangle - \langle f \rangle^2) = \frac{N-1}{N} \sigma^2$$

So, the unbiased estimate for σ^2 is

$$\sigma^2 \approx \frac{N}{N-1} \left(\overline{f^2} - (\bar{f})^2 \right)$$

Loss of one degree of freedom because sample variance is computed relative to sample mean rather than the true mean.

Examples of Unbiased and Biased Estimators

$$\begin{aligned} E_T &= \frac{\int d\mathbf{R} \psi_T(\mathbf{R}) \mathcal{H} \psi_T(\mathbf{R})}{\int d\mathbf{R} \psi_T^2(\mathbf{R})} = \int d\mathbf{R} \frac{\psi_T^2(\mathbf{R})}{\int d\mathbf{R} \psi_T^2(\mathbf{R})} \frac{\mathcal{H} \psi_T(\mathbf{R})}{\psi_T(\mathbf{R})} \\ &= \frac{1}{N} \sum_{i=1}^N \frac{\mathcal{H} \Psi_T(\mathbf{R}_i)}{\Psi_T(\mathbf{R}_i)} = \frac{1}{N} \sum_{i=1}^N E_L(\mathbf{R}_i) \quad \text{unbiased} \end{aligned}$$

$$\begin{aligned} E_T &= \frac{\int d\mathbf{R} \psi_T(\mathbf{R}) \mathcal{H} \psi_T(\mathbf{R})}{\int d\mathbf{R} \psi_T^2(\mathbf{R})} = \frac{\int d\mathbf{R} \frac{|\psi_T(\mathbf{R})|}{\int d\mathbf{R} |\psi_T(\mathbf{R})|} \operatorname{sgn}(\psi_T(\mathbf{R})) \mathcal{H} \psi_T(\mathbf{R})}{\int d\mathbf{R} \frac{|\psi_T(\mathbf{R})|}{\int d\mathbf{R} |\psi_T(\mathbf{R})|} |\psi_T(\mathbf{R})|} \\ &= \frac{\sum_{i=1}^N \operatorname{sgn}(\psi_T(\mathbf{R}_i)) \mathcal{H} \Psi_T(\mathbf{R}_i)}{\sum_{i=1}^N |\psi_T(\mathbf{R}_i)|} \quad \mathcal{O}\left(\frac{1}{N}\right) \text{ bias} \end{aligned}$$

Can do better by calculating covariances.

Unbiased Estimators to $\mathcal{O}(1/N)$ of functions of expectation values and their variance

$\langle x \rangle \equiv$ population averages of x , i.e., true expectation value

$\bar{x} \equiv$ average of x over sample of size N

Let F be a function of expectation values, $\{\langle f_i \rangle\}$.

$F(\{\bar{f}_i\})$ is unbiased estimator for $F(\{\langle f_i \rangle\})$ iff F is linear function of $\{\langle f_i \rangle\}$.

In general

$$F(\{\langle f_i \rangle\}) = \langle F(\{\bar{f}_i\}) \rangle - \frac{1}{2} \sum_{i,j} \frac{\partial^2 F}{\partial f_i \partial f_j} \frac{\text{cov}(f_i, f_j)}{N} + \mathcal{O}\left(\frac{1}{N^2}\right)$$

$$\text{var}(F(\{\langle f_i \rangle\})) = \sum_{i,j} \frac{\partial F}{\partial f_i} \frac{\partial F}{\partial f_j} \text{cov}(f_i, f_j) + \mathcal{O}\left(\frac{1}{N}\right)$$

Unbiased Estimators to $\mathcal{O}(1/N)$ or better (cont)

$$\text{Estim. of mean } \langle f \rangle_\rho = \bar{f}_\rho$$

$$\text{Estim. of variance } \langle f^2 \rangle_\rho - \langle f \rangle_\rho^2 = \frac{N}{N-1} (\bar{f}_\rho^2 - \bar{f}_\rho^2)$$

$$\text{Estim. of error of sample mean} = \sqrt{\frac{1}{N-1} (\bar{f}_\rho^2 - \bar{f}_\rho^2)}$$

$$\text{Estim. of covar. } \text{cov}(f, g) \equiv \langle fg \rangle_\rho - \langle f \rangle_\rho \langle g \rangle_\rho = \frac{N}{N-1} (\bar{fg}_\rho - \bar{f}_\rho \bar{g}_\rho)$$

$$\text{Estim. of product of expec. values } \langle f \rangle_\rho \langle g \rangle_\rho = \bar{f}_\rho \bar{g}_\rho - \frac{1}{N} \text{cov}(f, g)$$

$$\text{Estim. of ratio of expec. values } \frac{\langle f \rangle_\rho}{\langle g \rangle_\rho} \approx \frac{\bar{f}_\rho}{\bar{g}_\rho} \left[1 - \frac{1}{N} \left(\frac{\sigma_g^2}{\langle g \rangle_\rho^2} - \frac{\text{cov}(f, g)}{\langle f \rangle_\rho \langle g \rangle_\rho} \right) \right]$$

$$\text{Var}(\bar{f}_\rho \bar{g}_\rho) = \frac{1}{N} \langle f \rangle_\rho^2 \langle g \rangle_\rho^2 \left(\frac{\sigma_f^2}{\langle f \rangle_\rho^2} + \frac{\sigma_g^2}{\langle g \rangle_\rho^2} + 2 \frac{\text{cov}(f, g)}{\langle f \rangle_\rho \langle g \rangle_\rho} \right)$$

$$\text{Var}\left(\frac{\bar{f}_\rho}{\bar{g}_\rho}\right) = \frac{1}{N} \frac{\langle f \rangle_\rho^2}{\langle g \rangle_\rho^2} \left[\frac{\sigma_f^2}{\langle f \rangle_\rho^2} + \frac{\sigma_g^2}{\langle g \rangle_\rho^2} - 2 \frac{\text{cov}(f, g)}{\langle f \rangle_\rho \langle g \rangle_\rho} \right].$$

Note that the product, $\bar{f}_\rho \bar{g}_\rho$ is unbiased if $\text{cov}(f, g) = 0$, but the ratio $\frac{\bar{f}_\rho}{\bar{g}_\rho}$ has $\mathcal{O}(1/N)$ bias even if $\text{cov}(f, g) = 0$. The ratio has no bias (and no fluctuations) when f and g are perfectly correlated. In practice replace population means by sample means on RHS.

Unbiased Estimators of autocorrelated variables

Independent samples:

Estim. for error of sample mean $\overline{\Delta}_f = \sqrt{\frac{1}{N-1} (\overline{f}_\rho^2 - \overline{f}_\rho^2)}$

Autocorrelated samples (e.g. from Metropolis-Hastings):

Estim. for error of sample mean $\overline{\Delta}_f = \sqrt{\frac{1}{N_{\text{eff}} - 1} (\overline{f}_\rho^2 - \overline{f}_\rho^2)}$

where

$$N_{\text{eff}} = \frac{N}{(1 + 2\tau_f)} \equiv \frac{N}{T_{\text{corr}}}$$
$$\tau_f = \frac{\sum_{t=1}^{\infty} [\langle f_1 f_{1+t} \rangle_\rho - \langle f \rangle_\rho^2]}{\sigma_f^2}$$

If samples are indep., $\langle f_1 f_{1+t} \rangle_\rho = \langle f \rangle_\rho^2$ and **integrated autocorrelation time** $\tau_f = 0$. Since the relevant quantity for MC calculations is $(1 + 2\tau_f) \equiv T_{\text{corr}}$ we will refer to it as the **autocorrelation time of f** , though this is not standard usage.

Lecture 2

Variational Monte Carlo

W. L. McMillan, Phys. Rev. 138, A442 (1965) (Bosons)

D. Ceperley, G. V. Chester and M. H. Kalos, PRB 16, 3081 (1977) (Fermions)

Recap of Variational and Projector MC

$$E_V = \frac{\left[\sum_i^{N_{\text{MC}}} \left(\frac{t_i}{g_i} \right)^2 E_L(i) \right]_{\Psi_G}}{\left[\sum_k^{N_{\text{MC}}} \left(\frac{t_k}{g_k} \right)^2 \right]_{\Psi_G^2}} \quad (\text{Value depends on } \Psi_T, \text{ error } \Psi_T, \Psi_G)$$

$$E_0 = \frac{\left[\sum_i^{N_{\text{MC}}} \left(\frac{t_i}{g_i} \right) E_L(i) \right]_{\Psi_G \Psi_0}}{\left[\sum_k^{N_{\text{MC}}} \left(\frac{t_k}{g_k} \right) \right]_{\Psi_G \Psi_0}} \quad (\text{Value exact}^\dagger. \text{ Error depends on } \Psi_T, \Psi_G.)$$

$$E_L(i) = \frac{\sum_j^{N_{\text{st}}} H_{ij} t_j}{t_i}$$

In both VMC and PMC weighted average of the *configuration value of \hat{H}* aka *local energy, $E_L(i)$* , but from points sampled from different distributions.

This is practical for systems that are large enough to be interesting if

1. $t_i = \langle \phi_i | \Psi_T \rangle$, $g_i = \langle \phi_i | \Psi_G \rangle$ can be evaluated in polynomial time, say N^3
2. the sum in $E_L(i)$ can be done quickly, i.e., \hat{H} is sparse (if space discrete) or semi-diagonal (if space continuous).

gc) other details.

[†] In practice, usually necessary to make approximation (e.g. FN) and value depends on Ψ_G .

Recap of Variational Monte Carlo in Real Space

W. L. McMillan, Phys. Rev. **138**, A442 (1965)

Monte Carlo is used to perform the many-dimensional integrals needed to calculate quantum mechanical expectation values. e.g.

$$\begin{aligned} E_T &= \frac{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \mathcal{H} \psi_T(\mathbf{R})}{\int d\mathbf{R} \psi_T^2(\mathbf{R})} \\ &= \int d\mathbf{R} \frac{\psi_T^2(\mathbf{R})}{\int d\mathbf{R} \psi_T^2(\mathbf{R})} \frac{\mathcal{H} \psi_T(\mathbf{R})}{\psi_T(\mathbf{R})} \\ &= \frac{1}{N} \sum_i \frac{\mathcal{H} \Psi_T(\mathbf{R}_i)}{\Psi_T(\mathbf{R}_i)} = \frac{1}{N} \sum_i E_L(\mathbf{R}_i) \end{aligned}$$

Energy is obtained as an arithmetic sum of the *local energies* $E_L(\mathbf{R}_i)$ evaluated for configurations sampled from $\psi_T^2(\mathbf{R})$ using a generalization of the Metropolis method. If ψ_T is an eigenfunction the $E_L(\mathbf{R}_i)$ do not fluctuate. Accuracy of VMC depends crucially on the quality of $\psi_T(\mathbf{R})$.

Diffusion MC does better by projecting onto ground state.

Three ingredients for accurate Variational Monte Carlo

1. A method for sampling an arbitrary wave function [Metropolis-Hastings](#).
2. A functional form for the wave function that is capable of describing the correct physics/chemistry.
3. An efficient method for optimizing the parameters in the wave functions.

Metropolis-Hastings Monte Carlo

Metropolis, Rosenbluth², Teller², JCP, **21** 1087 (1953)

W.K. Hastings, Biometrika, **57** (1970)

Metropolis method originally used to sample the Boltzmann distribution. This is still one of its more common uses.

General method for sampling **any known discrete or continuous** density. (Other quantum Monte Carlo methods, e.g., diffusion MC, enable one to sample densities that are not explicitly known but are the eigenstates of known matrices or integral kernels.)

Metropolis-Hastings has serial correlations. Hence, direct sampling methods preferable, but rarely possible for complicated densities in many dimensions.

Metropolis-Hastings Monte Carlo (cont)

A *Markov chain* is specified by two ingredients:

- 1) an initial state
- 2) a transition matrix $M(\mathbf{R}_f|\mathbf{R}_i)$ (probability of transition $\mathbf{R}_i \rightarrow \mathbf{R}_f$.)

$$M(\mathbf{R}_f|\mathbf{R}_i) \geq 0, \quad \sum_{\mathbf{R}_f} M(\mathbf{R}_f|\mathbf{R}_i) = 1. \quad \text{Column-stochastic matrix}$$

To sample $\rho(\mathbf{R})$, start from an arbitrary \mathbf{R}_i and evolve the system by repeated application of M that satisfies the *stationarity condition* (flux into state \mathbf{R}_i equals flux out of \mathbf{R}_i):

$$\sum_{\mathbf{R}_f} M(\mathbf{R}_i|\mathbf{R}_f) \rho(\mathbf{R}_f) = \sum_{\mathbf{R}_f} M(\mathbf{R}_f|\mathbf{R}_i) \rho(\mathbf{R}_i) = \rho(\mathbf{R}_i) \quad \forall \mathbf{R}_i$$

i.e., $\rho(\mathbf{R})$ is a **right eigenvector** of M with eigenvalue 1.

Stationarity \Rightarrow if we start with ρ , will continue to sample ρ .

Want more than that: **any** initial density should evolve to ρ .

$$\lim_{n \rightarrow \infty} M^n(\mathbf{R}_f|\mathbf{R}_i) \delta(\mathbf{R}_i) = \rho(\mathbf{R}_f), \quad \forall \mathbf{R}_i.$$

i.e., ρ should be the **dominant** right eigenvector.

Metropolis-Hastings Monte Carlo (cont)

Want that **any** initial density should evolve to ρ .

$$\lim_{n \rightarrow \infty} M^n(\mathbf{R}_f | \mathbf{R}_i) \delta(\mathbf{R}_i) = \rho(\mathbf{R}_f), \quad \forall \mathbf{R}_i.$$

ρ should be the **dominant** right eigenvector. Additional conditions needed to guarantee this.

A nonnegative matrix M is said to be **primitive** if $\exists n$ such that M^n has all elements positive. (Can go from any state to any other in finite number of steps.)

(Special case of) **Perron-Frobenius Theorem**: A column-stochastic primitive matrix has a unique dominant eigenvalue of 1, with a positive right eigenvector and a left eigenvector with all components equal to 1 (by definition of column-stochastic matrix).

In practice, length of Monte Carlo should be long enough that there be a significant probability of the system making several transitions between the neighborhoods of any pair of representative states that make a significant contribution to the average. This ensures that states are visited with the correct probability with only small statistical fluctuations.

For example in a double-well system many transitions between the 2 wells should occur, but we can choose our proposal matrix to achieve this even if barrier between wells is high.

Metropolis-Hastings Monte Carlo (cont)

Construction of M

Need a prescription to construct M , such that ρ is its stationary state. Impose *detailed balance* condition

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

Detailed balance more stringent than stationarity condition (removed the sums).

Detailed balance is not necessary but provides way to construct M .

Write elements of M as product of elements of a proposal matrix T and an acceptance Matrix A ,

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

$M(\mathbf{R}_f|\mathbf{R}_i)$ and $T(\mathbf{R}_f|\mathbf{R}_i)$ are stochastic matrices, but $A(\mathbf{R}_f|\mathbf{R}_i)$ is not.

Detailed balance is now:

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

$$\text{or} \quad \frac{A(\mathbf{R}_f|\mathbf{R}_i)}{A(\mathbf{R}_i|\mathbf{R}_f)} = \frac{T(\mathbf{R}_i|\mathbf{R}_f) \rho(\mathbf{R}_f)}{T(\mathbf{R}_f|\mathbf{R}_i) \rho(\mathbf{R}_i)}.$$

Metropolis-Hastings Monte Carlo (cont)

Choice of Acceptance Matrix A

$$\frac{A(\mathbf{R}_f|\mathbf{R}_i)}{A(\mathbf{R}_i|\mathbf{R}_f)} = \frac{T(\mathbf{R}_i|\mathbf{R}_f) \rho(\mathbf{R}_f)}{T(\mathbf{R}_f|\mathbf{R}_i) \rho(\mathbf{R}_i)}.$$

Infinity of choices for A . Any function

$$F\left(\frac{T(\mathbf{R}_i|\mathbf{R}_f) \rho(\mathbf{R}_f)}{T(\mathbf{R}_f|\mathbf{R}_i) \rho(\mathbf{R}_i)}\right) = A(\mathbf{R}_f|\mathbf{R}_i)$$

for which $F(x)/F(1/x) = x$ and $0 \leq F(x) \leq 1$ will do.

Choice of Metropolis *et al.* $F(x) = \min\{1, x\}$, maximizes the acceptance:

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

Other less good choices for $A(\mathbf{R}_f|\mathbf{R}_i)$ have been made, e.g. $F(x) = \frac{x}{1+x}$

$$A(\mathbf{R}_f|\mathbf{R}_i) = \frac{T(\mathbf{R}_i|\mathbf{R}_f) \rho(\mathbf{R}_f)}{T(\mathbf{R}_i|\mathbf{R}_f) \rho(\mathbf{R}_f) + T(\mathbf{R}_f|\mathbf{R}_i) \rho(\mathbf{R}_i)}.$$

Metropolis: $T(\mathbf{R}_i|\mathbf{R}_f) = T(\mathbf{R}_f|\mathbf{R}_i)$, **Hastings:** $T(\mathbf{R}_i|\mathbf{R}_f) \neq T(\mathbf{R}_f|\mathbf{R}_i)$

Metropolis-Hastings Monte Carlo (cont)

Choice of Proposal Matrix T

So, the optimal choice for the acceptance matrix $A(\mathbf{R}_f|\mathbf{R}_i)$ is simple and known.

However, there is considerable scope for using one's ingenuity to come up with good proposal matrices, $T(\mathbf{R}_f|\mathbf{R}_i)$, that allow one to make large moves with large acceptances, in order to make the autocorrelation time small.

Choice of Proposal Matrix T in Metropolis-Hastings (cont)

CJU, PRL **71**, 408 (1993)

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

Use freedom in T to make $\frac{T(\mathbf{R}_i|\mathbf{R}_f) \rho(\mathbf{R}_f)}{T(\mathbf{R}_f|\mathbf{R}_i) \rho(\mathbf{R}_i)} \approx 1$.

$T(\mathbf{R}_f|\mathbf{R}_i) \propto \rho(\mathbf{R}_f)$ optimal if $T(\mathbf{R}_f|\mathbf{R}_i)$ can be sampled over all space – usually not the case. And if it is, then one would not use Metropolis-Hastings in the first place.

Otherwise, let
$$T(\mathbf{R}_f|\mathbf{R}_i) = \frac{S(\mathbf{R}_f|\mathbf{R}_i)}{\int d\mathbf{R}_f S(\mathbf{R}_f|\mathbf{R}_i)} \approx \frac{S(\mathbf{R}_f|\mathbf{R}_i)}{S(\mathbf{R}_i|\mathbf{R}_i)\Omega(\mathbf{R}_i)}$$

$S(\mathbf{R}_f|\mathbf{R}_i)$ is non-zero only in domain $D(\mathbf{R}_i)$ of volume $\Omega(\mathbf{R}_i)$ around \mathbf{R}_i).

$$\frac{A(\mathbf{R}_f, \mathbf{R}_i)}{A(\mathbf{R}_i, \mathbf{R}_f)} = \frac{T(\mathbf{R}_i|\mathbf{R}_f) \rho(\mathbf{R}_f)}{T(\mathbf{R}_f|\mathbf{R}_i) \rho(\mathbf{R}_i)} \approx \frac{\Omega(\mathbf{R}_i)}{\Omega(\mathbf{R}_f)} \frac{S(\mathbf{R}_i|\mathbf{R}_i)}{S(\mathbf{R}_f|\mathbf{R}_f)} \frac{S(\mathbf{R}_i|\mathbf{R}_f)}{S(\mathbf{R}_f|\mathbf{R}_i)} \frac{\rho(\mathbf{R}_f)}{\rho(\mathbf{R}_i)}$$

from which it is apparent that the choice

$$S(\mathbf{R}_f|\mathbf{R}_i) \approx \sqrt{\rho(\mathbf{R}_f)/\Omega(\mathbf{R}_f)} \quad \text{yields} \quad A(\mathbf{R}_f, \mathbf{R}_i)/A(\mathbf{R}_i, \mathbf{R}_f) \approx 1.$$

Choice of Proposal Matrix T in Metropolis-Hastings (cont)

To be more precise, if the log-derivatives of $T(\mathbf{R}_f|\mathbf{R}_i)$ equal those of $\sqrt{\rho(\mathbf{R}_f)/\Omega(\mathbf{R}_f)}$ at $\mathbf{R}_f = \mathbf{R}_i$, the average acceptance goes as $1 - \mathcal{O}(\Delta^m)$, where Δ is the linear dimension of $D(\mathbf{R}_i)$.

In general, $m=2$, but if $D(\mathbf{R}_i)$ is inversion symmetric with \mathbf{R}_i at its center, then $m=3$.

Considerable improvement compared to using a symmetric $S(\mathbf{R}_f|\mathbf{R}_i)$ or choosing $S(\mathbf{R}_f|\mathbf{R}_i) \propto \rho(\mathbf{R}_f)$ for either of which $m=1$.

Another possible choice, motivated by (DMC) is

$$T(\mathbf{R}_f|\mathbf{R}_i) = \frac{1}{(2\pi\tau)^{3/2}} \exp\left[\frac{-(\mathbf{R}_f - \mathbf{R}_i - \mathbf{V}(\mathbf{R}_i)\tau)^2}{2\tau}\right], \quad \mathbf{V}(\mathbf{R}_i) = \frac{\nabla\Psi(\mathbf{R}_i)}{\Psi(\mathbf{R}_i)}$$

Advantage: allows Metropolis Monte Carlo and diffusion Monte Carlo programs to share almost all the code.

$m = 1$ for this choice of T . Such an algorithm is more efficient than one with a symmetric $S(\mathbf{R}_f|\mathbf{R}_i)$ or one for which $S(\mathbf{R}_f|\mathbf{R}_i) \propto \rho(\mathbf{R}_f)$, but less efficient than one for which $S(\mathbf{R}_f|\mathbf{R}_i) \propto \sqrt{\rho(\mathbf{R}_f)/\Omega(\mathbf{R}_f)}$.

These arguments are rigorous only in the small-step limit and are applicable only to functions with sufficiently many derivatives within $D(\mathbf{R}_i)$. In practice these ideas yield large reduction in the autocorrelation time provided that we employ a coordinate system such that ρ has continuous derivatives within $D(\mathbf{R}_i)$.

Some examples

We want to sample from $|\Psi(\mathbf{R})|^2$.

We propose moves with probability density

$$T(\mathbf{R}_f|\mathbf{R}_i) = \frac{S(\mathbf{R}_f|\mathbf{R}_i)}{\int d\mathbf{R}_f S(\mathbf{R}_f|\mathbf{R}_i)} \approx \frac{S(\mathbf{R}_f|\mathbf{R}_i)}{S(\mathbf{R}_i|\mathbf{R}_i)\Omega(\mathbf{R}_i)}$$

and since the acceptance is

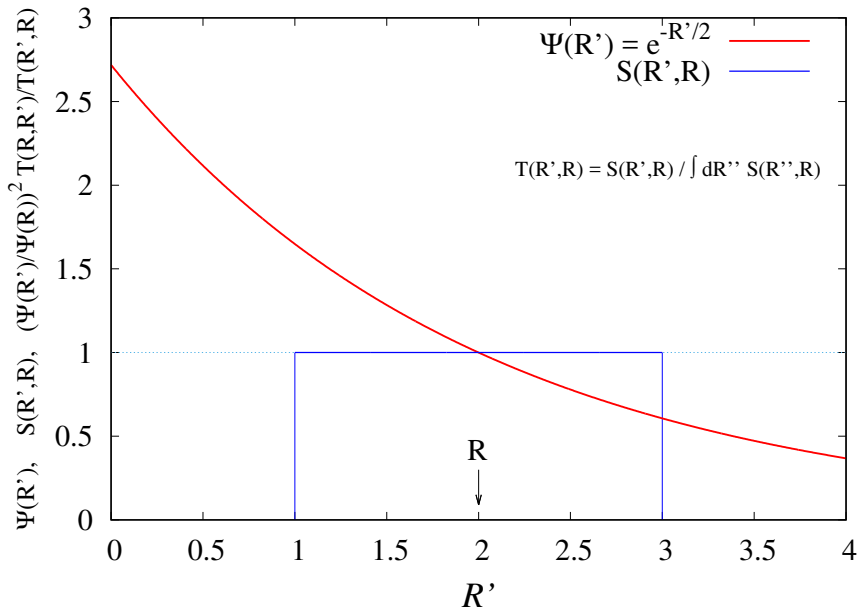
$$A(\mathbf{R}_f|\mathbf{R}_i) = \min \left\{ 1, \frac{|\Psi(\mathbf{R}_f)|^2 T(\mathbf{R}_i|\mathbf{R}_f)}{|\Psi(\mathbf{R}_i)|^2 T(\mathbf{R}_f|\mathbf{R}_i)} \right\}$$

we want

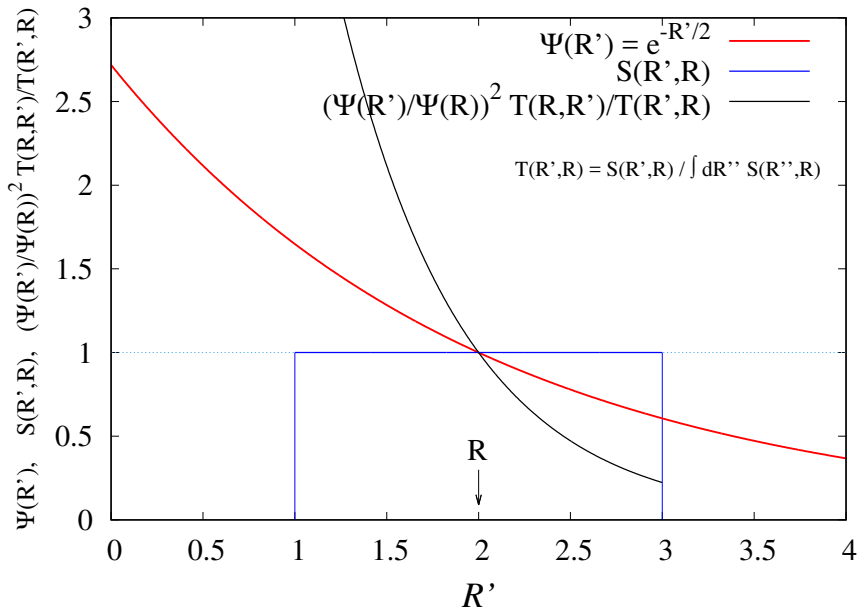
$$\frac{|\Psi(\mathbf{R}_f)|^2 T(\mathbf{R}_i|\mathbf{R}_f)}{|\Psi(\mathbf{R}_i)|^2 T(\mathbf{R}_f|\mathbf{R}_i)}$$

to be as close to 1 as possible.

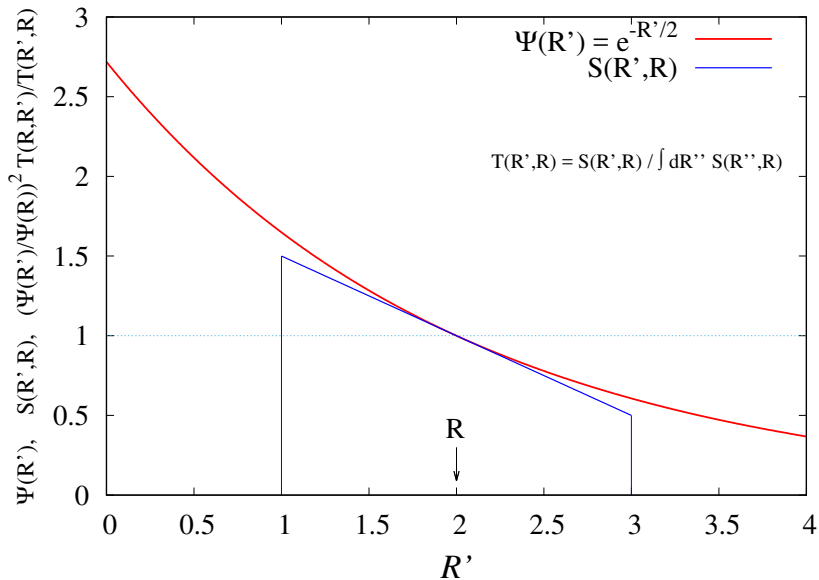
Symmetrical T in Metropolis



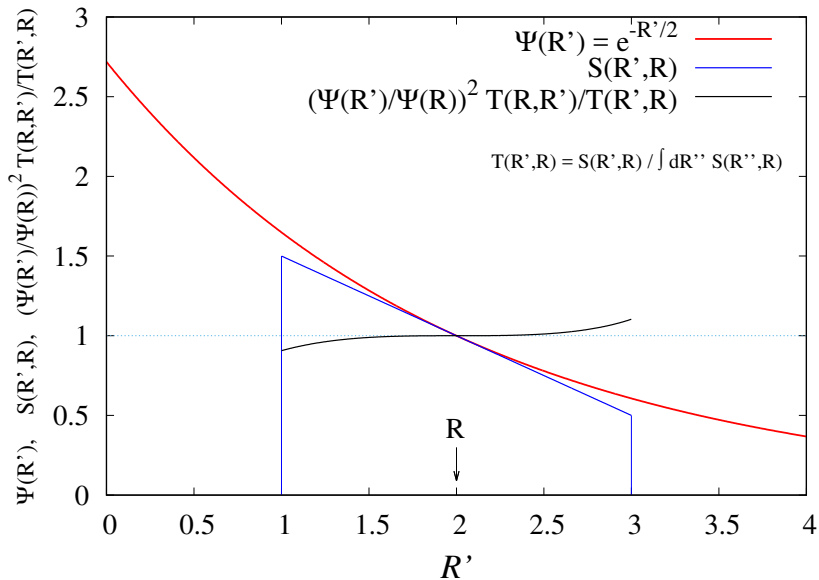
Symmetrical T in Metropolis



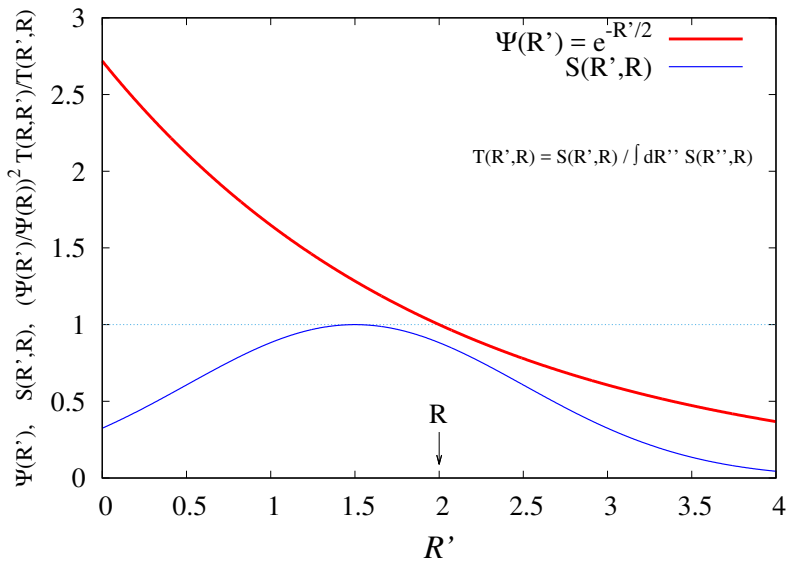
Non-symmetrical linear T in Metropolis-Hastings



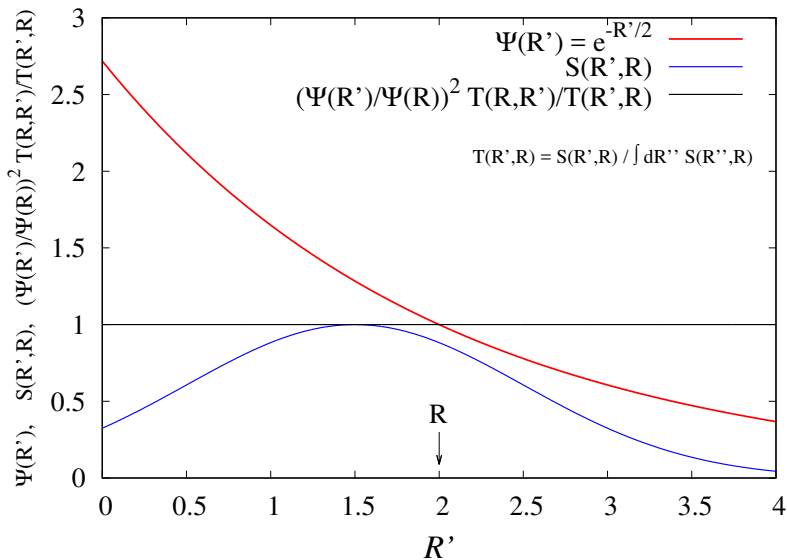
Non-symmetrical linear T in Metropolis-Hastings



Non-symmetrical drifted Gaussian T in Metropolis-Hastings

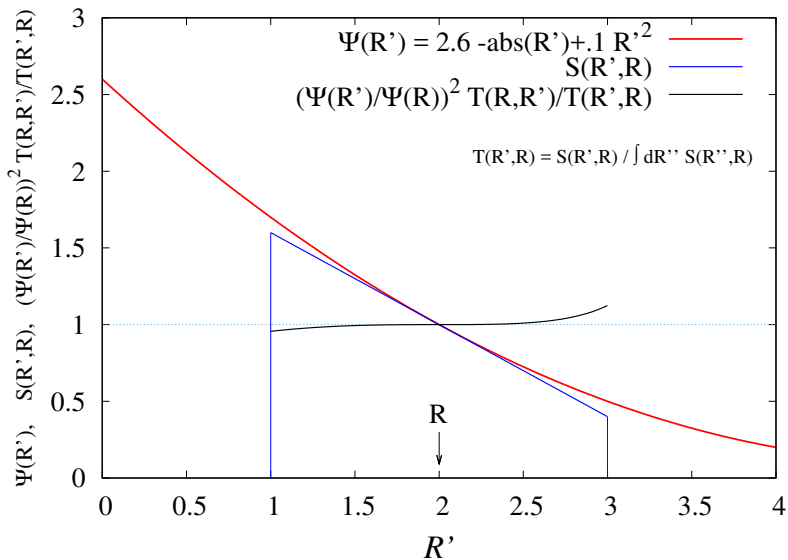


Non-symmetrical drifted Gaussian T in Metropolis-Hastings



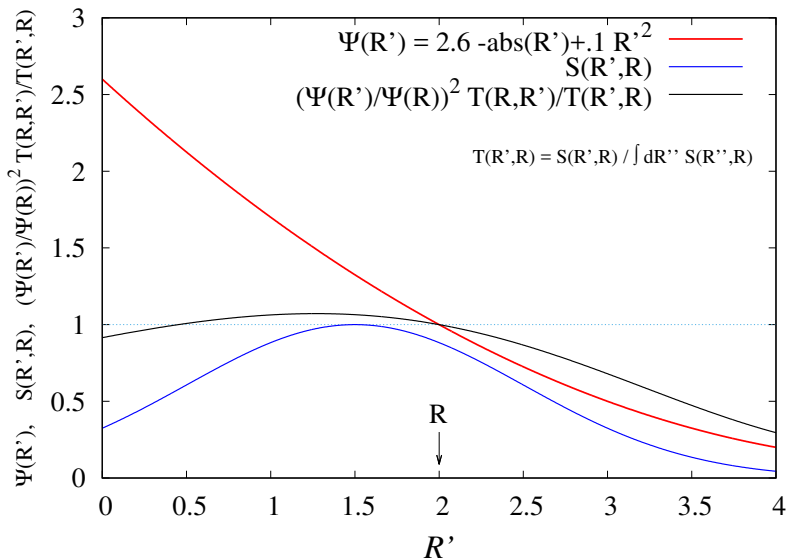
For this $\Psi(R')$, the drifted Gaussian gives perfect acceptance! Not generally true.

Non-symmetrical linear T in Metropolis-Hastings



The force-bias choice works just as well for this different function.

Non-symmetrical drifted Gaussian T in Metropolis-Hastings



For this $\Psi(R')$, the drifted Gaussian deviates from 1 linearly.

Choice of Proposal Matrix T in Metropolis-Hastings (cont)

When will the above not work so well?

What assumptions have we made in both of the non-symmetric choices above?

Choice of Proposal Matrix T in Metropolis-Hastings (cont)

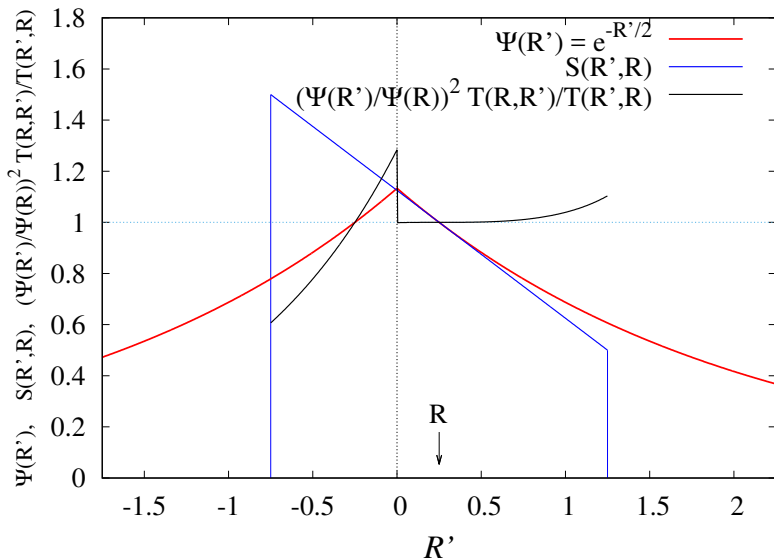
When will the above not work so well?

What assumptions have we made in both of the non-symmetric choices above?

Answer: In both cases we are utilizing the gradient of the function to be sampled and are implicitly assuming that it is smooth.

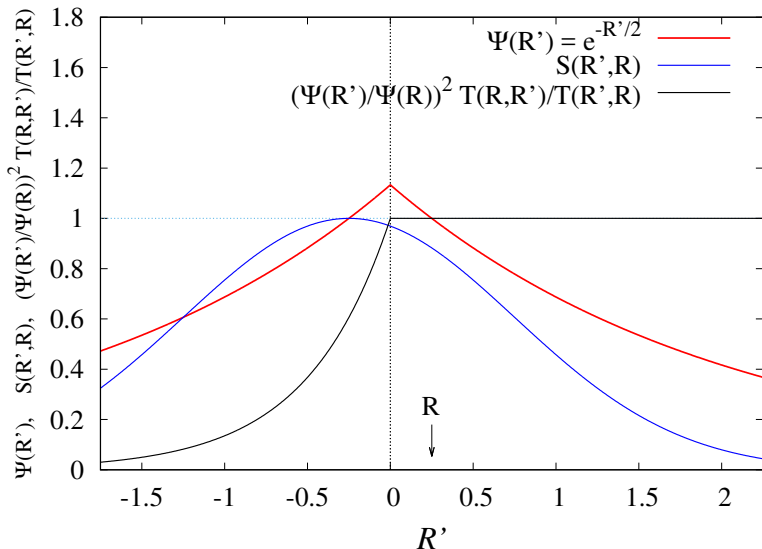
Let's see what happens when it is not.

Non-symmetrical linear T in Metropolis-Hastings



When the gradient has a discontinuity the acceptance goes down.

Non-symmetrical drifted Gaussian T in Metropolis-Hastings



When the gradient has a discontinuity the acceptance goes down.

The drifted-Gaussian even overshoots the nucleus.

Choice of Proposal Matrix T in Metropolis-Hastings (cont)

How to make large moves with high acceptance in spite of wavefunctions that have cusps at nuclei?

1. Make moves in spherical polar coordinates, centered on the nearest nucleus.
2. Radial move is proportional to distance to nucleus, say in interval $[\frac{r}{5}, 5r]$.
3. Angular move gets *larger* as electron approaches nucleus.

Using these ideas an autocorrelation time $T_{\text{corr}} \approx 1$ can be achieved!

Details are in: [Accelerated Metropolis Method](#), C. J. Umrigar, PRL **71** 408, (1993).

The point of the above exercise was not the particular problem treated, but rather to provide a concrete example of the ideas that enable making large moves with high acceptance, thereby achieving $T_{\text{corr}} \approx 1$.

Metropolis-Hastings Monte Carlo (cont)

Some Observations about Metropolis-Hastings Method

1. To sample states with relative density ρ it is not necessary to know the normalization of ρ . Metropolis automatically samples $\rho(\mathbf{R}_i) / \int d\mathbf{R}_f \rho(\mathbf{R}_f)$. So, it is useful for calculating quantities of the form

$$\frac{\int d\mathbf{R}_i e(\mathbf{R}_i) \rho(\mathbf{R}_i)}{\int d\mathbf{R}_f \rho(\mathbf{R}_f)}$$

which is the form encountered in quantum mechanics and statistical mechanics.

(Can also be used to calculate $\int d\mathbf{R}_i f(\mathbf{R}_i)$, with importance sampling provided one has a $g(\mathbf{R}_i)$ that mimics $f(\mathbf{R}_i)$ but whose integral is known. Of course if in addition $g(\mathbf{R}_i)$ can be sampled directly then one would not use Metropolis, so this is rarely useful.)

2. The variance of the estimate for the expectation value $\langle X \rangle$ is given by

$$\frac{1}{N/T_{\text{CORR}} - 1} \left(\frac{\sum X(\mathbf{R}_i)^2}{N} - \left(\frac{\sum X(\mathbf{R}_i)}{N} \right)^2 \right).$$

That is, the effective number of configurations N_{eff} is smaller than N by a factor of T_{CORR} , which we define to be the autocorrelation time.

($T_{\text{CORR}} = 1 + 2t_{\text{CORR}}$, where $t_{\text{CORR}} = \sum_i^\infty \rho_i$ is the integrated autocorrelation time.)

Metropolis-Hastings Monte Carlo (cont)

Some Observations about Metropolis-Hastings Method

3. The rate of convergence to the desired density and the autocorrelation time of estimates of observables is governed by the sub-dominant eigenvalues of M . In practice reduce T_{corr} by inventing large moves that have large acceptance probabilities.
4. Folklore: when one can choose the range of the PDF from which moves are proposed the optimal one has an average acceptance close to 0.5. Reasonable choice in absence of any information, but in fact the optimal choice may have an average acceptance that is anywhere between zero and one.

I have found instances where the optimum is as small as 0.2 or as large as 0.9.

A much better criterion is to maximize the rate at which the system diffuses through configuration space $\langle A(\mathbf{R}_f|\mathbf{R}_i)(\mathbf{R}_f - \mathbf{R}_i)^2 \rangle$.

The real measure of goodness is of course to minimize the autocorrelation time for the observables of interest.

Estimation of Errors

Autocorrelation time

N Monte Carlo steps = N_b blocks \times N_s steps/block

If N_b is large enough the block averages are nearly independent.

\bar{E} = average of E_L over the N Monte Carlo steps

σ = rms fluctuations of individual E_L

σ_b = rms fluctuations of block averages of E_L

Need to estimate T_{corr} to make sure $N_b \gg T_{\text{corr}}$.

$N_{\text{eff}} = N/T_{\text{corr}}$ independent measurements of E_L , so get T_{corr} from:

$$\text{err}(\bar{E}) = \frac{\sigma}{\sqrt{N_b \times N_s}} \sqrt{T_{\text{corr}}} = \frac{\sigma_b}{\sqrt{N_b}}$$

\Rightarrow

$$T_{\text{corr}} = N_s \left(\frac{\sigma_b}{\sigma} \right)^2$$

Choose $N_s \gg T_{\text{corr}}$, say, $100 T_{\text{corr}}$.

If $N_s \approx 10 T_{\text{corr}}$, T_{corr} underest. $\approx 10\%$.

Blocking Analysis for error of mean of autocorrelated variables

Flyvberg and Peterson, JCP 1979

Compute recursively and plot

$$\frac{1}{N_b(N_b - 1)} \sum_{i=1}^{N_b} (m_i - \bar{E})^2$$

for various blocking levels, $N_s = 1, 2, 2^2, 2^3, \dots, N/2$

If the variables were uncorrelated to begin with then these estimates of the error would be equal aside from statistical fluctuations, which would increase with blocking level.

If they are autocorrelated, the estimated error will grow and the flatten out when the block means become uncorrelated, which can only happen if $N \gg T_{\text{corr}}$.

Assuming that block means are independent Gaussian variables (they are not at the lower blocking levels), the estimated uncertainty of the error is

$$\frac{\sqrt{2} (\text{error estim})}{\sqrt{(N_b - 1)}}$$

since the PDF of the sum of squares of $N_b - 1$ normal standard deviates is $\chi^2(N_b - 1)$ and has variance $2(N_b - 1)$. So, cannot go to very large N_s (N_b small).

A reasonable choice of blocking level is the highest one for which the increase in the estimate for the error is larger than the increase in the estimate for the error in the error. It is possible to get a somewhat better estimate by predicting the shape of the curve and extrapolating when say $N < 1000 T_{\text{corr}}$.

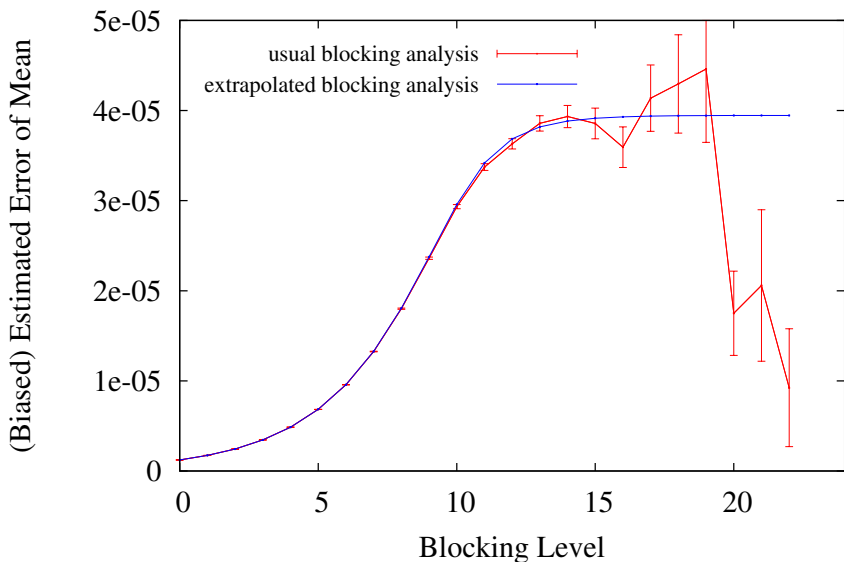
Blocking Analysis for error of mean of autocorrelated variables

In variational Monte Carlo, T_{corr} is usually very small if one makes an intelligent choice for the proposal matrix. With the algorithm we typically use $T_{\text{corr}} < 2$ even for systems with say 100 electrons!

However, in some of the projector Monte Carlo methods (e.g. FCIQMC), T_{corr} can be much larger, even for much smaller systems. Further, in these methods one needs to use a large population of walkers, so it becomes expensive to have a large number of Monte Carlo steps. In the next viewgraph, a blocking analysis for a run with $T_{\text{corr}} \approx 1000$ and $N = 2^{23}$ is shown.

Blocking Analysis for error of mean of autocorrelated variables

Blocking Analysis of error of run with $N=2^{23}$



Functional form of Trial Wave Function

Other methods: Restrictions on the form of the wavefn.:

1. Many-body wavefn. expanded in determinants of single-particle orbitals.
2. Single-particle orbitals are expanded in planewaves or gaussians.
occasionally wavelets etc.

QMC: Great freedom in form of the wavefn. – use physics/chemistry intuition:

1. Multideterminant times Jastrow. Ceperley, many others
2. Antisymmetrized Geminal Power times Jastrow. Sorella, Casula
$$\mathcal{A} \left[\Phi(\mathbf{r}_1^\uparrow, \mathbf{r}_1^\downarrow) \Phi(\mathbf{r}_2^\uparrow, \mathbf{r}_2^\downarrow) \cdots \Phi(\mathbf{r}_{N/2}^\uparrow, \mathbf{r}_{N/2}^\downarrow) \right]$$
3. Pfaffians times Jastrow. Schmidt, Mitas, Wagner and coworkers
$$\mathcal{A} [\Phi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) \Phi(\mathbf{r}_3, s_3; \mathbf{r}_4, s_4) \cdots \Phi(\mathbf{r}_{N-1}, s_{N-1}; \mathbf{r}_N, s_N)]$$
4. Backflow times Jastrow. Needs and coworkers, Moroni (extension of Feynman)
5. Laughlin and Composite Fermion. Jeon, Güclu, CJU and Jain

Multideterminant \times Jastrow form of Trial Wavefunction

$$\psi_T = \left(\sum_n d_n D_n^\uparrow D_n^\downarrow \right) \times \mathcal{J}(r_i, r_j, r_{ij})$$

- **Determinants:** $\sum_n d_n D_n^\uparrow D_n^\downarrow$

D^\uparrow and D^\downarrow are determinants of single-particle orbitals ϕ for up (\uparrow) and down (\downarrow) spin electrons respectively.

The single-particle orbitals ϕ are given by:

$$\phi(\mathbf{r}_i) = \sum_{\alpha k} c_{k\alpha} N_{k\alpha} r_{i\alpha}^{n_{k\alpha}-1} e^{-\zeta_{k\alpha} r_{i\alpha}} Y_{l_{k\alpha} m_{k\alpha}}(\hat{\mathbf{r}}_{i\alpha})$$

- **Jastrow:** $\mathcal{J}(r_i, r_j, r_{ij}) = \prod_{\alpha i} \exp(A_{\alpha i}) \prod_{ij} \exp(B_{ij}) \prod_{\alpha ij} \exp(C_{\alpha ij})$
 - $A_{\alpha i} \Rightarrow$ electron-ion correlation $\sim N_{\text{atomtype}}$ of \mathcal{J} parms.
 - $B_{ij} \Rightarrow$ electron-electron correlation $\sim N_{\text{atomtype}}$ of $\zeta_{k\alpha}$ parms.
 - $C_{\alpha ij} \Rightarrow$ electron-electron-ion correlation $\sim N_{\text{atom}}^2$ of $c_{k\alpha}$ parms.
 - $\sim e^{N_{\text{atom}}}$ of d_n parms.

d_n , $c_{k\alpha}$, $\zeta_{k\alpha}$ and parms in \mathcal{J} are optimized.

Power of QMC:

\mathcal{J} parms. replace many d_n parms.

Cusp-conditions of Trial Wave Functions

Jastrow factor and divergences in the potential

At interparticle coalescence points, the potential diverges as

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

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

Want local energy $\frac{\mathcal{H}\Psi}{\Psi} = -\frac{1}{2} \sum_i \frac{\nabla_i^2 \Psi}{\Psi} + \mathcal{V}$ to be finite (const. for Ψ_0)

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

Cusp-conditions of Trial Wave Functions

Divergence in potential and behavior of the local energy

Consider two particles of masses m_i , m_j and charges q_i , q_j

Assume $r_{ij} \rightarrow 0$ while all other particles are well separated

Keep only diverging terms in $\frac{\mathcal{H}\Psi}{\Psi}$ and go to relative coordinates

close to $\mathbf{r} = \mathbf{r}_{ij} = 0$

$$\begin{aligned} -\frac{1}{2\mu_{ij}} \frac{\nabla^2 \Psi}{\Psi} + \mathcal{V}(r) &\sim -\frac{1}{2\mu_{ij}} \frac{\Psi''}{\Psi} - \frac{1}{\mu_{ij}} \frac{1}{r} \frac{\Psi'}{\Psi} + \mathcal{V}(r) \\ &\sim \boxed{-\frac{1}{\mu_{ij}} \frac{1}{r} \frac{\Psi'}{\Psi} + \mathcal{V}(r)} \end{aligned}$$

where $\mu_{ij} = m_i m_j / (m_i + m_j)$

Cusp-conditions of Trial Wave Functions

Divergence in potential and cusp conditions

Diverging terms in the local energy

$$-\frac{1}{\mu_{ij}} \frac{1}{r} \frac{\Psi'}{\Psi} + \mathcal{V}(r) = -\frac{1}{\mu_{ij}} \frac{1}{r} \frac{\Psi'}{\Psi} + \frac{q_i q_j}{r} = \text{finite}$$

$\Rightarrow \Psi$ must satisfy Kato's cusp conditions:

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

where $\hat{\Psi}$ is a spherical average

Note: We assumed $\Psi(r_{ij} = 0) \neq 0$.

Slightly more involved derivation if $\Psi(r_{ij} = 0) = 0$ (parallel spins).

Cusp-conditions of Trial Wave Functions

Cusp conditions: example

The condition for the local energy to be finite at $r = 0$ is

$$\frac{\Psi'}{\Psi} = \mu_{ij} q_i q_j$$

• Electron-nucleus: $\mu = 1, q_i = 1, q_j = -Z \Rightarrow$

$$\left. \frac{\Psi'}{\Psi} \right|_{r=0} = -Z$$

• Electron-electron($\uparrow\downarrow$): $\mu = \frac{1}{2}, q_i = 1, q_j = 1 \Rightarrow$

$$\left. \frac{\Psi'}{\Psi} \right|_{r=0} = 1/2$$

▷ Electron-nucleus cusps imposed on combination of the determinantal part (using Slater basis functions) and the e-n Jastrow.

Jastrow Factors

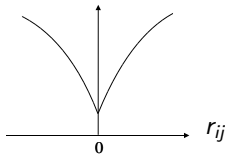
- ▷ Electron-electron cusps imposed by the Jastrow factor

Example: Simple Jastrow factor

$$\mathcal{J}(r_{ij}) = \prod_{i < j} \exp \left\{ \frac{b_1 r_{ij}}{1 + b_2 r_{ij}} \right\}$$

with $b_1^{\uparrow\downarrow} = \frac{1}{2}$ or $b_1^{\uparrow\uparrow} = b_1^{\downarrow\downarrow} = \frac{1}{4}$

Imposes cusp conditions
+
keeps electrons apart



Comments on Jastrow factor

▷ Electron-electron-nucleus terms C

The Jastrow does not change the nodes of the wavefunction.

If the order of the polynomial in the e-e-n terms is infinite, Ψ can exactly describe a two-electron atom or ion in 1S ground state

For the He atom, a 6th-order polynomial gives energies good to better than $1 \mu\text{Ha}$, or 99.998% of the correlation energy, $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$

▷ Is this Jastrow factor adequate for multi-electron systems?

The e-e-n terms are the most important: due to the exclusion principle, it is rare for 3 or more electrons to be close, since at least 2 electrons must necessarily have the same spin

Higher-order Jastrow factors

Jastrow factor with e-e, e-e-n and e-e-e-n terms

	\mathcal{J}	E_{VMC}	$E_{\text{VMC}}^{\text{corr}}$ (%)	σ_{VMC}
Li	E_{HF}	-7.43273	0	
	e-e	-7.47427(4)	91.6	0.240
	+ e-e-n	-7.47788(1)	99.6	0.037
	+ e-e-e-n	-7.47797(1)	99.8	0.028
	E_{exact}	-7.47806	100	0
Ne	E_{HF}	-128.5471	0	
	e-e	-128.713(2)	42.5	1.90
	+ e-e-n	-128.9008(1)	90.6	0.90
	+ e-e-e-n	-128.9029(3)	91.1	0.88
	E_{exact}	-128.9376	100	0

Huang, Umrigar, Nightingale, J. Chem. Phys. **107**, 3007 (1997)

Static and Dynamic Correlation

Dynamic and static correlation

$\Psi = \text{Jastrow} \times \text{Determinants} \rightarrow$ Two types of correlation

▷ Dynamic correlation

Due to inter-electron repulsion

Always present

Efficiently described by Jastrow factor

▷ Static correlation

Due to near-degeneracy of occupied and unoccupied orbitals

Not always present

Efficiently described by a linear combination of determinants (change nodes of Ψ)

Static and Dynamic Correlation

Example: Be atom has $2s$ - $2p$ near-degeneracy, prototypical example of static correlation

HF ground state configuration



Additional important configuration



Ground state has 1S symmetry \Rightarrow 4 determinants:

$$D = (1s^\uparrow, 2s^\uparrow, 1s^\downarrow, 2s^\downarrow) +$$

$$c \left[(1s^\uparrow, 2p_x^\uparrow, 1s^\downarrow, 2p_x^\downarrow) + (1s^\uparrow, 2p_y^\uparrow, 1s^\downarrow, 2p_y^\downarrow) + (1s^\uparrow, 2p_z^\uparrow, 1s^\downarrow, 2p_z^\downarrow) \right]$$

$$1s^2 2s^2 \quad \times \mathcal{J}(r_{ij}) \quad \rightarrow E_{\text{VMC}}^{\text{corr}} = 61\%$$

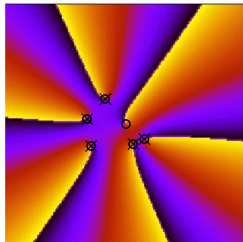
$$1s^2 2s^2 \quad \times \mathcal{J}(r_{ij}, r_{\alpha i}, r_{\alpha j}) \quad \rightarrow E_{\text{VMC}}^{\text{corr}} = 80\%$$

$$1s^2 2s^2 \oplus 1s^2 2p^2 \quad \times \mathcal{J}(r_{ij}, r_{\alpha i}, r_{\alpha j}) \quad \rightarrow E_{\text{VMC}}^{\text{corr}} = 99.3\%$$

Wavefunctions for Hole in a Filled Landau Level

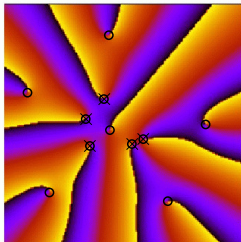
6 electrons in a harmonic well and a magnetic field.

5 electrons are fixed. Phase of the wavefunction is plotted as the 6th moves.



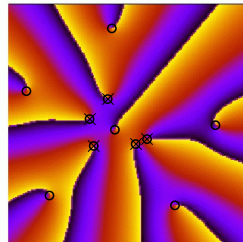
Vortex hole

$$E = 4.293$$



Composite-fermion

$$E = 4.265$$



Exact diagonalization

$$E = 4.264$$

Jeon, Güclu, CJU, Jain, PRB 2005

Optimization of many-body wavefunctions

Standard methods do not work for the wavefunctions we are interested in. For example, they work for linear combinations of determinants but not for linear combinations of determinants multiplied by a Jastrow factor. Issues:

1. Many nonlinear parameters
2. Optimization in the presence of stochastic noise

But is it a worthwhile expenditure of effort to optimize wavefunctions?

Almost all errors reduced by optimizing trial wavefunctions

1. Statistical error (both the rms fluctuations of E_L and the autocorrelation time)
2. E_{VMC}
3. Fixed-node error in E_{DMC} (nodes move during optimization). Fixed node errors can be **LARGE**. For C_2 , FN error for 1-det wavefn is 1.3 eV for total energy and 0.7 eV for well-depth. However, optimized multidet. wavefn has FN error that is better than chemical accuracy (1 kcal/mole = 0.043 eV/molecule).
4. Time-step error in DMC
5. Population control error in DMC
6. Pseudopotential locality error in DMC when using nonlocal pseudopotentials
7. Error of observables that do not commute with the Hamiltonian (mixed estimators, $\langle \Psi_0 | \hat{A} | \Psi_T \rangle$ not exact even for nodeless ψ_0, ψ_T) if one does not use forward/side walking.

Choices to be made when optimizing trial wavefunctions

1. What precisely do we want to optimize – the objective function or measure of goodness?
2. What method do we use to do the optimization? If more than one method is applied to the same objective function, they will of course give the same wavefunction, but the efficiency with which we arrive at the solution may be much different.
3. When we test to see if the proposed new parameters are better than the old ones, do we test on a fixed sample of MC points or draw new MC points each time?

Measures of goodness of variational wave functions

$$\min E_{\text{VMC}} = \frac{\langle \psi_{\text{T}} | H | \psi_{\text{T}} \rangle}{\langle \psi_{\text{T}} | \psi_{\text{T}} \rangle} = \langle E_{\text{L}} \rangle_{|\psi_{\text{T}}|^2}$$

$$\min \sigma_{\text{VMC}}^2 = \frac{\langle \psi_{\text{T}} | (H - E_{\text{T}})^2 | \psi_{\text{T}} \rangle}{\langle \psi_{\text{T}} | \psi_{\text{T}} \rangle} = \langle E_{\text{L}}^2(\mathbf{R}_i) \rangle_{|\psi_{\text{T}}|^2} - \langle E_{\text{L}}(\mathbf{R}_i) \rangle_{|\psi_{\text{T}}|^2}^2$$

$$\max \Omega^2 = \frac{|\langle \psi_{\text{FN}} | \psi_{\text{T}} \rangle|^2}{\langle \psi_{\text{FN}} | \psi_{\text{FN}} \rangle \langle \psi_{\text{T}} | \psi_{\text{T}} \rangle} = \frac{\left\langle \frac{\psi_{\text{FN}}}{\psi_{\text{T}}} \right\rangle_{|\psi_{\text{T}}|^2}^2}{\left\langle \left| \frac{\psi_{\text{FN}}}{\psi_{\text{T}}} \right|^2 \right\rangle_{|\psi_{\text{T}}|^2}}$$

$$\min E_{\text{DMC}} = \frac{\langle \psi_{\text{FN}} | H | \psi_{\text{T}} \rangle}{\langle \psi_{\text{FN}} | \psi_{\text{T}} \rangle} = \langle E_{\text{L}} \rangle_{|\psi_{\text{FN}} \psi_{\text{T}}|}$$

For an infinitely flexible wave function all optimizations will yield the exact wavefunction (except that minimizing σ could yield an excited state) but for the imperfect functional forms used in practice they differ.

Progress in optimization of Many-Body Wavefunctions

Naive energy optim. → Variance optim. → Efficient energy optim.

- 1988 naive energy optimization, few (~ 3) parameters
- 1988 – 2001 variance optimization, ~ 100 parameters
could be used for more, but, variance does not couple strongly to some parameters
- 2001 – 2012 efficient energy optimization, ~ 1000 's of parameters
- 2012 – 2017 efficient energy optimization, $\sim 100,000$'s of parameters

Most recent advance: Assaraf, Moroni, Filippi, arXiv 2017.

Optimization of Many-Body Wavefunctions

A major advantage of quantum Monte Carlo methods is that there is no restriction on the form of $\psi_T(\mathbf{R})$. Hence any insight one may have, as regards the nature of the many-body correlations, can be built into $\psi_T(\mathbf{R})$ and tested. To exploit this freedom it is necessary to have a method for optimizing arbitrary wavefunctions.

First thought: Minimize the energy on MC sample.

$$\bar{E} = \sum_{i=1}^{N_{\text{conf}}} \frac{\mathcal{H}\psi_T(\mathbf{R}_i; \{p\})}{\psi_T(\mathbf{R}_i; \{p\})} w_i, \quad w_i = \left| \frac{\psi_T(\mathbf{R}_i)}{\psi_T^0(\mathbf{R}_i)} \right|^2 / \sum_{i=1}^{N_{\text{conf}}} \left| \frac{\psi_T(\mathbf{R}_i)}{\psi_T^0(\mathbf{R}_i)} \right|^2$$

Second thought: Minimize the variance of the local energy.

$$\sigma^2 = \sum_{i=1}^{N_{\text{conf}}} \left(\frac{\mathcal{H}\psi_T(\mathbf{R}_i; \{p\})}{\psi_T(\mathbf{R}_i; \{p\})} - \bar{E} \right)^2 w_i$$

Third thought: Minimize the energy using MC but not on MC sample.
What is meant by this will become clear later.

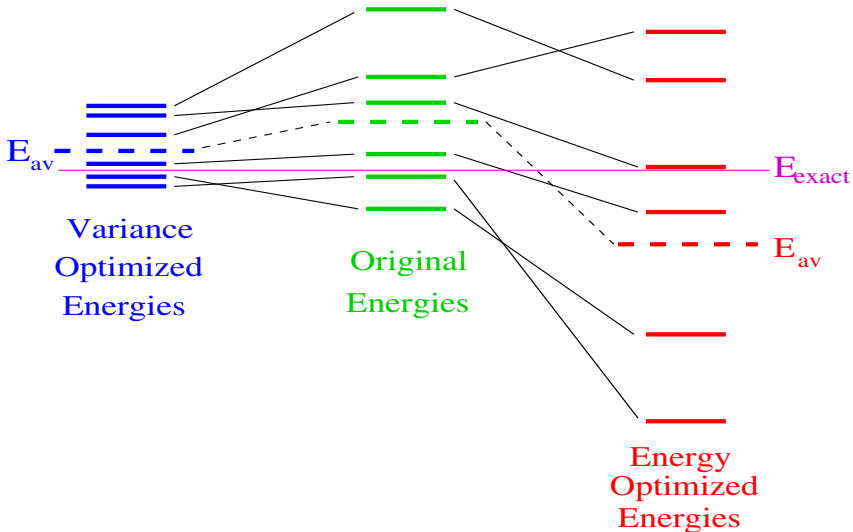
Variance

vs.

Energy

$$\sigma^2 = \sum_{i=1}^{N_{\text{conf}}} \left(\frac{\mathcal{H}\Psi_T(\mathbf{R}_i)}{\Psi_T(\mathbf{R}_i)} - \bar{E} \right)^2$$

$$\bar{E} = \sum_{i=1}^{N_{\text{conf}}} \frac{\mathcal{H}\Psi_T(\mathbf{R}_i)}{\Psi_T(\mathbf{R}_i)}$$



Take-home Message

Energy optimization methods that minimize the energy evaluated on finite sample will yield poor energies on other samples, unless the sample used to do the minimization is very large.

So, efficient energy optimization methods do **NOT** optimize the energy evaluated on a finite sample, although they **do** minimize the energy in the limit of an infinite sample.

Advantages of Energy (or Mixed) Optim. vs. Variance Optim.

1. Want lowest energy; fluctuations are of secondary importance. Energy and variance do not always go hand-in-hand enough.
2. Some parameters couple more strongly to energy than variance.
3. Some variance-optimized parameters make wave function too extended.
4. Hellman-Feynman theorem can be used for forces (when combined with variance reduction methods).

Variational energy optimization methods

1. **Newton method** CJU, Filippi, PRL 94, 150201 (2005):

Add terms to the Hessian that contribute nothing in the limit of an infinite MC sample, but cancel much of the fluctuations for a finite MC sample.

Gain in efficiency: 3 orders of magnitude for NO_2 , more for $\text{C}_{10}\text{H}_{12}$ compared to Newton of Lin-Zhang-Rappe.

2. **Linear method (generalized eigenvalue problem):**

1 **Linear parameters:** Nightingale, et al., PRL, **87**, 043401 (2001)

Use asymmetric H to have zero variance property in the limit that the basis functions span an invariant subspace.

2 **Nonlinear parameters:** Toulouse, CJU, J. Chem. Phys., (2007, 2008). CJU, Toulouse, Filippi, Sorella, Hennig, PRL **98**, 110201 (2007).

Choose freedom of normalization $\Psi(\mathbf{p}, \mathbf{R}) = N(\mathbf{p}) \Phi(\mathbf{p}, \mathbf{R})$ to make a near optimal change in the parameters.

3. **Perturbation theory in an arbitrary nonorthog. basis:**

Toulouse, CJU, J. Chem. Phys., **126**, 084102 (2007).

(Small modification of Scemama-Filippi (2006) perturbative EFP, modification of the Fahy-Filippi-Prendergast-Schautz EFP method.)

4. **Stochastic Reconfiguration:**

Sorella, Casula, Rocca, J. Chem. Phys., **127**, 014105 (2007).

Although it requires more iterations than 1) and 2), it is well suited for very large numbers of parameters.

Newton Method

Calculate gradient \mathbf{g} and Hessian \mathbf{h} of objective function and update parameters:

$$\mathbf{p}_{\text{next}} = \mathbf{p}_{\text{current}} - \mathbf{h}^{-1}\mathbf{g}$$

or more efficiently ($\mathcal{O}(N_p^2)$ vs. $\mathcal{O}(N_p^3)$) find parameter changes, $\delta\mathbf{p}$, by solving linear equations:

$$\mathbf{h} \delta\mathbf{p} = -\mathbf{g},$$

Optimization of Jastrow and determinantal parameters encounter different problems.

Jastrow: For the form of the Jastrow we use and the systems we study the eigenvalues of the Hessian span 10-12 orders of magnitude. So using steepest descent is horribly slow and using the Hessian, or a reasonable approximation to it, is essential even if there were no statistical noise.

determinantal: The eigenvalues of the Hessian span only 1-2 orders of magnitude. However, the Hessian has terms involving

$$\frac{\frac{\partial\psi}{\partial p_i}}{\psi}$$

that diverge as $\psi \rightarrow 0$. The strongest divergence among various terms cancels.

Energy Minimization via Newton

Lin, Zhang, Rappe, JCP 2000; CJU, Filippi, PRL 2005

$$\bar{E} = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \langle E_L \rangle_{\psi^2}; \quad E_L(\mathbf{R}) = \frac{H\psi(\mathbf{R})}{\psi(\mathbf{R})}$$

Energy gradient components, \bar{E}_i :

$$\begin{aligned} \bar{E}_i &= \frac{\langle \psi_i | H \psi \rangle + \langle \psi | H \psi_i \rangle}{\langle \psi | \psi \rangle} - 2 \frac{\langle \psi | H | \psi \rangle \langle \psi | \psi_i \rangle}{\langle \psi | \psi \rangle^2} \\ &= \frac{\langle \psi_i | H \psi \rangle + \langle \psi | H \psi_i \rangle}{\langle \psi | \psi \rangle} - 2 \frac{\bar{E} \langle \psi | \psi_i \rangle}{\langle \psi | \psi \rangle} = 2 \frac{\langle \psi_i | H \psi \rangle - \bar{E} \langle \psi | \psi_i \rangle}{\langle \psi | \psi \rangle} \quad (\text{by Hermiticity}) \\ &= \left\langle \frac{\psi_i}{\psi} E_L + \frac{H \psi_i}{\psi} - 2 \bar{E} \frac{\psi_i}{\psi} \right\rangle_{\psi^2} = 2 \left\langle \frac{\psi_i}{\psi} (E_L - \bar{E}) \right\rangle_{\psi^2} \quad (\text{MC expression}) \end{aligned}$$

Is blue or green expression better for MC?

Energy Minimization via Newton

Lin, Zhang, Rappe, JCP 2000; CJU, Filippi, PRL 2005

$$\bar{E} = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \langle E_L \rangle_{\psi^2}; \quad E_L(\mathbf{R}) = \frac{H\psi(\mathbf{R})}{\psi(\mathbf{R})}$$

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Is blue or green expression better for MC?

Green is better because it is a zero-variance expression in the limit that ψ is the exact ground state (CJU, Filippi, PRL 2005) Moreover it is simpler and faster.

Energy Minimization via Newton

CJU, Filippi, PRL 2005

Energy hessian components, E_{ij} :

$$\begin{aligned}\bar{E}_i &= 2 \frac{\langle \psi_i | H \psi \rangle - \bar{E} \langle \psi | \psi_i \rangle}{\langle \psi | \psi \rangle} \equiv 2 \frac{\langle \psi_i | \psi (E_L - \bar{E}) \rangle}{\langle \psi^2 \rangle} \\ E_{ij} &= 2 \left[\frac{\langle (\psi_{ij} \psi + \psi_i \psi_j) (E_L - \bar{E}) \rangle + \langle \psi_i \psi (E_{L,j} - \bar{E}_j) \rangle - \bar{E}_i \langle \psi \psi_j \rangle}{\langle \psi^2 \rangle} \right] \\ &= 2 \left[\left\langle \left(\frac{\psi_{ij}}{\psi} + \frac{\psi_i \psi_j}{\psi^2} \right) (E_L - \bar{E}) \right\rangle_{\psi^2} - \left\langle \frac{\psi_i}{\psi} \right\rangle_{\psi^2} \bar{E}_j - \left\langle \frac{\psi_j}{\psi} \right\rangle_{\psi^2} \bar{E}_i + \left\langle \frac{\psi_i}{\psi} E_{L,j} \right\rangle_{\psi^2} \right].\end{aligned}$$

What can be done to improve this expression?

Energy Minimization via Newton

CJU, Filippi, PRL 2005

Energy hessian components, E_{ij} :

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What can be done to improve this expression?

1) Symmetrize – but this does not reduce fluctuations much

Energy Minimization via Newton

CJU, Filippi, PRL 2005

Energy hessian components, E_{ij} :

$$\begin{aligned}\bar{E}_i &= 2 \frac{\langle \psi_i | H \psi \rangle - \bar{E} \langle \psi | \psi_i \rangle}{\langle \psi | \psi \rangle} \equiv 2 \frac{\langle \psi_i | \psi (E_L - \bar{E}) \rangle}{\langle \psi^2 \rangle} \\ E_{ij} &= 2 \left[\frac{\langle (\psi_{ij} \psi + \psi_i \psi_j) (E_L - \bar{E}) \rangle + \langle \psi_i \psi (E_{L,j} - \bar{E}_j) \rangle - \bar{E}_i \langle \psi \psi_j \rangle}{\langle \psi^2 \rangle} \right] \\ &= 2 \left[\left\langle \left(\frac{\psi_{ij}}{\psi} + \frac{\psi_i \psi_j}{\psi^2} \right) (E_L - \bar{E}) \right\rangle_{\psi^2} - \left\langle \frac{\psi_i}{\psi} \right\rangle_{\psi^2} \bar{E}_j - \left\langle \frac{\psi_j}{\psi} \right\rangle_{\psi^2} \bar{E}_i + \left\langle \frac{\psi_i}{\psi} E_{L,j} \right\rangle_{\psi^2} \right].\end{aligned}$$

What can be done to improve this expression?

1) Symmetrize – but this does not reduce fluctuations much

2) Noting that $\langle E_{L,j} \rangle_{\psi^2} = \frac{\langle \psi^2 \left(\frac{H\psi}{\psi} \right)_j \rangle}{\langle \psi^2 \rangle} = \frac{\langle \psi^2 \left(\frac{H\psi_j}{\psi} - \frac{\psi_j}{\psi^2} H\psi \right) \rangle}{\langle \psi^2 \rangle} = \frac{\langle \psi H \psi_j - \psi_j H \psi \rangle}{\langle \psi^2 \rangle} = 0$

by hermiticity of \hat{H} , and, that the fluctuations of the covariance $\langle ab \rangle - \langle a \rangle \langle b \rangle$ are smaller than those of the product $\langle ab \rangle$, when $\sqrt{\langle a^2 \rangle - \langle a \rangle^2} \ll |\langle a \rangle|$ and $\langle b \rangle = 0$ on ∞ sample but $\langle b \rangle \neq 0$ on finite sample, replace

$$\left\langle \frac{\psi_i}{\psi} E_{L,j} \right\rangle_{\psi^2} \rightarrow \frac{1}{2} \left(\left\langle \frac{\psi_i}{\psi} E_{L,j} \right\rangle_{\psi^2} - \left\langle \frac{\psi_i}{\psi} \right\rangle_{\psi^2} \langle E_{L,j} \rangle_{\psi^2} + \left\langle \frac{\psi_j}{\psi} E_{L,i} \right\rangle_{\psi^2} - \left\langle \frac{\psi_j}{\psi} \right\rangle_{\psi^2} \langle E_{L,i} \rangle_{\psi^2} \right)$$

3) Too hard to describe here.

Cyrus J. Umrigar

Energy Minimization via Newton

$$\begin{aligned}
 \bar{E}_{ij} &= 2 \left[\left\langle \left(\frac{\psi_{ij}}{\psi} + \frac{\psi_i \psi_j}{\psi^2} \right) (E_L - \bar{E}) \right\rangle_{\psi^2} - \left\langle \frac{\psi_i}{\psi} \right\rangle_{\psi^2} \bar{E}_j - \left\langle \frac{\psi_j}{\psi} \right\rangle_{\psi^2} \bar{E}_i \right] \\
 &\quad + \left\langle \frac{\psi_i}{\psi} E_{L,j} \right\rangle_{\psi^2} - \left\langle \frac{\psi_i}{\psi} \right\rangle_{\psi^2} \langle E_{L,j} \rangle_{\psi^2} + \left\langle \frac{\psi_j}{\psi} E_{L,i} \right\rangle_{\psi^2} - \left\langle \frac{\psi_j}{\psi} \right\rangle_{\psi^2} \langle E_{L,i} \rangle_{\psi^2} \\
 &= 2 \left[\left\langle \left(\frac{\psi_{ij}}{\psi} - \frac{\psi_i \psi_j}{\psi^2} \right) (E_L - \bar{E}) \right\rangle_{\psi^2} \quad (0 \text{ for } p_i \text{ linear in exponent}) \right. \\
 &\quad \left. + 2 \left\langle \left(\frac{\psi_i}{\psi} - \left\langle \frac{\psi_i}{\psi} \right\rangle_{\psi^2} \right) \left(\frac{\psi_j}{\psi} - \left\langle \frac{\psi_j}{\psi} \right\rangle_{\psi^2} \right) (E_L - \bar{E}) \right\rangle_{\psi^2} \right] \\
 &\quad + \left\langle \frac{\psi_i}{\psi} E_{L,j} \right\rangle_{\psi^2} - \left\langle \frac{\psi_i}{\psi} \right\rangle_{\psi^2} \langle E_{L,j} \rangle_{\psi^2} + \left\langle \frac{\psi_j}{\psi} E_{L,i} \right\rangle_{\psi^2} - \left\langle \frac{\psi_j}{\psi} \right\rangle_{\psi^2} \langle E_{L,i} \rangle_{\psi^2} .
 \end{aligned}$$

- 1) **Blue** and **green** terms are zero variance estimators.
- 2) **Red** terms are not, but, the terms we added in $=0$ for infinite sample and cancel most of the fluctuations for a finite sample.

Linear method for linear parameters

If all parameters are linear, i.e., $\psi = \sum_i p_i \psi_i$, then optimize using generalized eigenvalue equation, $\mathbf{H}\mathbf{p} = E\mathbf{S}\mathbf{p}$.

Symmetric or nonsymmetric H?

1) true \mathbf{H} is symmetric:

$$\text{True } H_{ij} = \int d^{3N}\mathbf{R} \psi_i(\mathbf{R}) \hat{H} \psi_j(\mathbf{R}) \quad \text{symmetric}$$

$$\text{MC estim. } H_{ij} = \sum_{n=1}^{N_{\text{MC}}} \frac{\psi_i(\mathbf{R}_n)}{\psi(\mathbf{R}_n)} \left(\frac{\hat{H}\psi_j(\mathbf{R}_n)}{\psi(\mathbf{R}_n)} \right) \quad \text{nonsymmetric}$$

$$\text{MC estim. } H_{ij} = \frac{1}{2} \sum_{n=1}^{N_{\text{MC}}} \left(\frac{\psi_i(\mathbf{R}_n)}{\psi(\mathbf{R}_n)} \frac{\hat{H}\psi_j(\mathbf{R}_n)}{\psi(\mathbf{R}_n)} + \frac{\hat{H}\psi_i(\mathbf{R}_n)}{\psi(\mathbf{R}_n)} \frac{\psi_j(\mathbf{R}_n)}{\psi(\mathbf{R}_n)} \right) \quad \text{symmetric}$$

Linear method for linear parameters

If all parameters are linear, i.e., $\psi = \sum_i p_i \psi_i$, then optimize using generalized eigenvalue equation, $\mathbf{H}\mathbf{p} = E\mathbf{S}\mathbf{p}$.

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$$\text{MC estim. } H_{ij} = \frac{1}{2} \sum_{n=1}^{N_{\text{MC}}} \left(\frac{\psi_i(\mathbf{R}_n)}{\psi(\mathbf{R}_n)} \frac{\hat{H}\psi_j(\mathbf{R}_n)}{\psi(\mathbf{R}_n)} + \frac{\hat{H}\psi_i(\mathbf{R}_n)}{\psi(\mathbf{R}_n)} \frac{\psi_j(\mathbf{R}_n)}{\psi(\mathbf{R}_n)} \right) \quad \text{symmetric}$$

2) Minimizing the energy evaluated on a finite sample, i.e., minimizing the Rayleigh quotient, $\partial E / \partial p_k = 0$, even with nonsymmetric H evaluated on finite sample, gives generalized eigenvalue equation with symmetric \mathbf{H} :

$$E = \min_{\mathbf{p}} \frac{\mathbf{p}^T \mathbf{H} \mathbf{p}}{\mathbf{p}^T \mathbf{S} \mathbf{p}} = \min_{\mathbf{p}} \frac{\sum_{ij} p_i H_{ij} p_j}{\sum_{ij} p_i S_{ij} p_j}$$

$$\frac{\partial E}{\partial p_k} = 0 \implies \left(\sum_{ij} p_i S_{ij} p_j \right) \left(\sum_j H_{kj} p_j + \sum_i p_i H_{ik} \right) - \left(\sum_{ij} p_i H_{ij} p_j \right) \left(2 \sum_j S_{kj} p_j \right) = 0$$

$$\frac{(\mathbf{H} + \mathbf{H}^T)}{2} \mathbf{p} = E \mathbf{S} \mathbf{p}$$

Nonsymm. H satisfies strong zero-variance principle

M. P. Nightingale and Melik-Alaverdian, PRL, **87**, 043401 (2001).

Nightingale's strong zero-variance principle:

If the states $\psi_i(\mathbf{R})$ are closed under \hat{H} then the values of the optimized parameters using nonsymmetric H_{ij} are independent of the MC sample, provided $N_{\text{MC}} \geq N_p$.

Proof: If closed $\exists \{p_j\}$ s.t.
$$\hat{H} \sum_{j=1}^{N_p} p_j |\psi_j\rangle = E \sum_{j=1}^{N_p} p_j |\psi_j\rangle$$

$\times \langle \psi_i | \mathbf{R}_n \rangle \langle \mathbf{R}_n | / \langle \psi | \mathbf{R}_n \rangle^2$ and sum over N_{MC} pts. (not complete sum over \mathbf{R} states), sampled from $|\psi(\mathbf{R})|^2$:

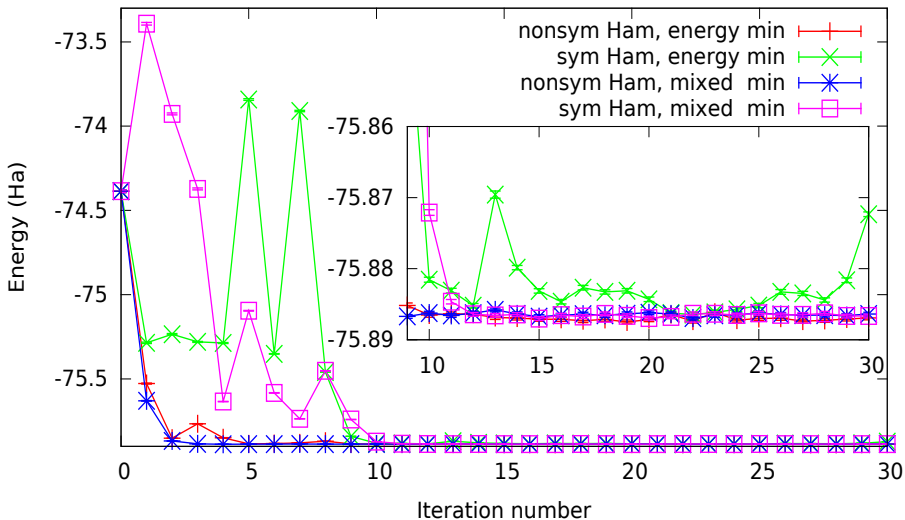
$$\sum_{j=1}^{N_p} p_j \underbrace{\sum_{n=1}^{N_{\text{MC}}} \frac{\langle \psi_i | \mathbf{R}_n \rangle \langle \mathbf{R}_n | \hat{H} | \psi_j \rangle}{\langle \psi | \mathbf{R}_n \rangle \langle \mathbf{R}_n | \psi \rangle}}_{H_{ij}} = E \sum_{j=1}^{N_p} p_j \underbrace{\frac{\sum_{n=1}^{N_{\text{MC}}} \langle \psi_i | \mathbf{R}_n \rangle \langle \mathbf{R}_n | \psi_j \rangle}{\langle \psi | \mathbf{R}_n \rangle \langle \mathbf{R}_n | \psi \rangle}}_{S_{ij}}$$

$$\sum_{i=1}^{N_p} H_{ij} p_j = E \sum_{i=1}^{N_p} S_{ij} p_j$$

H is nonsymmetric H of previous slide. Becomes symmetric when $\sum \rightarrow \int$.

Convergence of energy with symmetric and nonsymmetric Hamiltonians

Convergence of VMC energy of C_2 with optimization iterations



Linear method for nonlinear parameters

Toulouse, CJU, JCP (2007,2008); CJU et al., PRL, **87**, 043401 (2007).

Make linear-order Taylor expansion of Ψ (use $\Psi_i = \partial\Psi/\partial p_i$ as basis):

$$\Psi_{\text{lin}} = \Psi_0 + \sum_{i=0}^{N_{\text{parm}}} \Delta p_i \Psi_i, \quad (\text{Normalization: } \Delta p_0 = 1)$$

$\Psi_0 \equiv \Psi(\mathbf{p}_0, \mathbf{R})$ = current wave function

Ψ_{lin} = next linearized wave function

Ψ_i = derivative of Ψ at \mathbf{p}_0 , wrt i^{th} parameter.

No unique way to obtain new nonlinear parameters.

The simplest procedure: is $p_i^{\text{new}} = p_i + \Delta p_i$. Will not work in general. What can one do?

More complicated procedure: fit wave function form to optimal linear combination.

Simpler, yet efficient approach, freedom of norm to make linear approximation better

$$\begin{aligned}\bar{\Psi}(\mathbf{p}, \mathbf{R}) &= N(\mathbf{p}) \Psi(\mathbf{p}, \mathbf{R}), \quad N(\mathbf{p}_0) = 1 \\ \bar{\Psi}_i(\mathbf{p}_0, \mathbf{R}) &= \Psi_i(\mathbf{p}_0, \mathbf{R}) + N_i(\mathbf{p}_0) \Psi(\mathbf{p}_0, \mathbf{R})\end{aligned}$$

Note, $N_i = 0$ for linear parameters by definition. (If normal. depends on p_i , it is not linear.)

Dependence of parameter changes on normalization

Toulouse, CJU, JCP (2007,2008); CJU et al., PRL, **87**, 043401 (2007).

$$\begin{aligned}\bar{\Psi}(\mathbf{p}, \mathbf{R}) &= N(\mathbf{p}) \Psi(\mathbf{p}, \mathbf{R}), \quad N(\mathbf{p}_0) = 1 \\ \bar{\Psi}_i &= \Psi_i + N_i \Psi_0\end{aligned}$$

$$\Psi = \Psi_0 + \sum_{i=1}^{N_{\text{parm}}} \delta p_i \Psi_i$$

$$\bar{\Psi} = \Psi_0 + \sum_{i=1}^{N_{\text{parm}}} \delta \bar{p}_i \bar{\Psi}_i = \left(1 + \sum_{i=1}^{N_{\text{parm}}} N_i \delta \bar{p}_i \right) \Psi_0 + \sum_{i=1}^{N_{\text{parm}}} \delta \bar{p}_i \Psi_i$$

Since Ψ and $\bar{\Psi}$ are the optimal linear combin., they are the same aside from normalization

$$\delta p_i = \frac{\delta \bar{p}_i}{1 + \sum_{i=1}^{N_{\text{parm}}} N_i \delta \bar{p}_i} \implies \delta \bar{p}_i = \frac{\delta p_i}{1 - \sum_{i=1}^{N_{\text{parm}}} N_i \delta p_i}. \quad (1)$$

One can get $\delta \bar{p}_i$ directly from solving the eigenvalue problem in the renormalized basis or get δp_i from eigenvalue problem in the original basis and use the above transformation. In either case, use $\delta \bar{p}_i$ to update the parameters, $p_i^{\text{new}} = p_i + \delta \bar{p}_i$.

The denominator in Eq. 1 can be +ve, -ve or zero! So, predicted parameter changes can change sign depending on normalization!! If all parm. linear, $\delta \bar{p}_i = \delta p_i$, since all $N_i = 0$.

General semiorthogonalization

How to choose N_i ?

Toulouse, CJU, JCP (2007,2008); CJU et al., PRL, **87**, 043401 (2007).

$$\bar{\Psi}(\mathbf{p}, \mathbf{R}) = N(\mathbf{p}) \Psi(\mathbf{p}, \mathbf{R}), \quad N(\mathbf{p}_0) = 1$$

$$\bar{\Psi}_i = \Psi_i + N_i \Psi_0$$

Choose N_i such that the $\bar{\Psi}_i$ are orthogonal to a linear combination of Ψ_0 and Ψ_{lin} .

$$\left\langle \xi \frac{\Psi_0}{|\Psi_0|} + s(1 - \xi) \frac{\Psi_{\text{lin}}}{|\Psi_{\text{lin}}|} \middle| \Psi_i + N_i \Psi_0 \right\rangle = 0$$

Solving for N_i we get [$s = 1(-1)$ if $\langle \Psi_0 | \Psi_{\text{lin}} \rangle = 1 + \sum_j S_{0j} \Delta p_j > 0 (< 0)$],

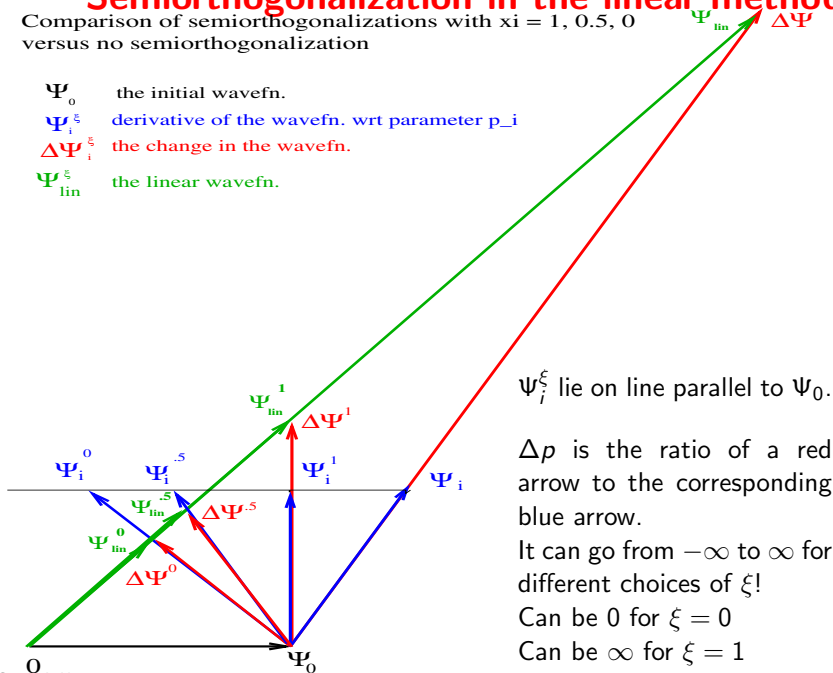
$$N_i = - \frac{\xi D S_{0i} + s(1 - \xi)(S_{0i} + \sum_j S_{ij} \Delta p_j)}{\xi D + s(1 - \xi)(1 + \sum_j S_{0j} \Delta p_j)}$$

where $D = \frac{|\Psi_{\text{lin}}|}{|\Psi_0|} = \left(1 + 2 \sum_j S_{0j} \Delta p_j + \sum_{i,j} S_{ij} \Delta p_i \Delta p_j \right)^{1/2}$

Semiorthogonalization in the linear method

Comparison of semiorthogonalizations with $\xi = 1, 0.5, 0$ versus no semiorthogonalization

- Ψ_0 the initial wavefn.
- Ψ_i^ξ derivative of the wavefn. wrt parameter p_i
- $\Delta\Psi_i^\xi$ the change in the wavefn.
- Ψ_{lin}^ξ the linear wavefn.



Ψ_i^ξ lie on line parallel to Ψ_0 .

Δp is the ratio of a red arrow to the corresponding blue arrow.

It can go from $-\infty$ to ∞ for different choices of ξ !

Can be 0 for $\xi = 0$

Can be ∞ for $\xi = 1$

Semiorthogonalization in the linear method

Ψ_0 is the initial wave function, Ψ_i^ζ is the derivative of the wave function wrt parameter p_i for ζ . If superscript ζ is omitted that denotes that no semiorthogonalization is done. Then

$$\Psi_{\text{lin}} = \Psi_0 + \sum_{i=1}^{N_{\text{param}}} \Delta \Psi_i^\zeta = \Psi_0 + \sum_{i=1}^{N_{\text{param}}} \Delta p_i^\zeta \Psi_i^\zeta, \quad \Delta p_i^\zeta = \frac{\Delta \Psi_i^\zeta}{\Psi_i^\zeta}$$

Note that $\|\Delta \Psi^\zeta\|$ is smallest for $\zeta = 1$ and that $\|\Psi_{\text{lin}}^{0.5}\| = \|\Psi_0\|$.

Also note that when there is just 1 parameter (can be generalized to > 1):

1. In the limit that $\Psi_{\text{lin}} \parallel \Psi_i$, $\Delta p_i = \pm \infty$
2. In the limit that $\Psi_{\text{lin}} \perp \Psi_0$, $\Delta p_i^1 = \pm \infty$ because $\Delta \Psi^1 = \infty$, and, $\Delta p_i^0 = 0$ because $\Psi_i^0 = \infty$
3. $\Delta p_i^{0.5}$ is always finite

Note that Δp_i^ζ decreases as ζ decreases from 1 to 0. In Fig. 1, Δp_i is > 1 for $\zeta = 1$, and, < 1 for $\zeta = 0.5, 0$.

Also note that in Fig. 1 if we rotate Ψ_{lin} such that $\frac{\nabla \Psi \cdot \Psi_0}{\|\nabla \Psi\| \|\Psi_0\|} > \frac{\Psi_{\text{lin}} \cdot \Psi_0}{\|\Psi_{\text{lin}}\| \|\Psi_0\|}$

then Δp_i has the opposite sign as Δp_i^ζ !

Variance Minimization via Linear method

Toulouse, CJU, J. Chem. Phys., **128**, 174101 (2008)

Can one use the linear method to optimize the variance?

Variance Minimization via Linear method

Toulouse, CJU, J. Chem. Phys., 128, 174101 (2008)

Can one use the linear method to optimize the variance?

Suppose we have some quadratic model of the energy variance to minimize

$$V_{\min} = \min_{\Delta \mathbf{p}} \left\{ V_0 + \mathbf{g}_V^T \cdot \Delta \mathbf{p} + \frac{1}{2} \Delta \mathbf{p}^T \cdot \mathbf{h}_V \cdot \Delta \mathbf{p} \right\}, \quad (2)$$

where $V_0 = \langle \bar{\Psi}_0 | (\hat{H} - E_0)^2 | \bar{\Psi}_0 \rangle$ is the energy variance of the current wave function $|\bar{\Psi}_0\rangle$, \mathbf{g}_V is the gradient of the energy variance with components $g_{V,i} = 2 \langle \bar{\Psi}_i | (\hat{H} - E_0)^2 | \bar{\Psi}_0 \rangle$ and \mathbf{h}_V is some approximation to the Hessian matrix of the energy variance. Then, one could instead minimize the following rational quadratic model (*augmented hessian method*)

$$V_{\min} = \min_{\Delta \mathbf{p}} \frac{\begin{pmatrix} 1 & \Delta \mathbf{p}^T \end{pmatrix} \begin{pmatrix} V_0 & \mathbf{g}_V^T/2 \\ \mathbf{g}_V/2 & \mathbf{h}_V/2 + V_0 \bar{\mathbf{S}} \end{pmatrix} \begin{pmatrix} 1 \\ \Delta \mathbf{p} \end{pmatrix}}{\begin{pmatrix} 1 & \Delta \mathbf{p}^T \end{pmatrix} \begin{pmatrix} 1 & \mathbf{0}^T \\ \mathbf{0} & \bar{\mathbf{S}} \end{pmatrix} \begin{pmatrix} 1 \\ \Delta \mathbf{p} \end{pmatrix}},$$

which agrees with the quadratic model in Eq. (2) up to second order in $\Delta \mathbf{p}$, and which leads to the following generalized eigenvalue equation

$$\begin{pmatrix} V_0 & \mathbf{g}_V^T/2 \\ \mathbf{g}_V/2 & \mathbf{h}_V/2 + V_0 \bar{\mathbf{S}} \end{pmatrix} \begin{pmatrix} 1 \\ \Delta \mathbf{p} \end{pmatrix} = V_{\min} \begin{pmatrix} 1 & \mathbf{0}^T \\ \mathbf{0} & \bar{\mathbf{S}} \end{pmatrix} \begin{pmatrix} 1 \\ \Delta \mathbf{p} \end{pmatrix}.$$

Hence, we can use linear method to optimize a linear combination of energy and variance!

Connection between Linear and Newton methods

Toulouse, CJU, J. Chem. Phys., **128**, 174101 (2008)

In semiorthogonal basis with $\xi = 1$, linear eqs. are:

$$\begin{pmatrix} E_0 & \mathbf{g}^T/2 \\ \mathbf{g}/2 & \bar{\mathbf{H}} \end{pmatrix} \begin{pmatrix} 1 \\ \Delta\mathbf{p} \end{pmatrix} = E_{\text{lin}} \begin{pmatrix} 1 & \mathbf{0}^T \\ \mathbf{0} & \bar{\mathbf{S}} \end{pmatrix} \begin{pmatrix} 1 \\ \Delta\mathbf{p} \end{pmatrix}, \quad (3)$$

Defining, $\Delta E = E_{\text{lin}} - E_0 \leq 0$, the 1st and 2nd eqs. are:

$$2\Delta E = \mathbf{g}^T \cdot \Delta\mathbf{p}, \quad 1^{\text{st}} \text{ eq.} \quad (4)$$

$$\frac{\mathbf{g}}{2} + \bar{\mathbf{H}}\Delta\mathbf{p} = E_{\text{lin}}\bar{\mathbf{S}}\Delta\mathbf{p} \quad 2^{\text{nd}} \text{ eq.} \quad (5)$$

$$\text{i.e., } 2(\bar{\mathbf{H}} - E_{\text{lin}}\bar{\mathbf{S}})\Delta\mathbf{p} = -\mathbf{g}, \quad (6)$$

This can be viewed as the Newton method with an approximate hessian, $\mathbf{h} = 2(\bar{\mathbf{H}} - E_{\text{lin}}\bar{\mathbf{S}})$ which is nonnegative definite. (It has all nonnegative eigenvalues since we are subtracting out the lowest eigenvalue.) This also means that the linear method can be stabilized in much the same way as the Newton method.

Note that $2(\bar{\mathbf{H}} - E_{\text{lin}}\bar{\mathbf{S}}) = 2(\bar{\mathbf{H}} - E_0\bar{\mathbf{S}} - \Delta E\bar{\mathbf{S}})$ and $2(\bar{\mathbf{H}} - E_0\bar{\mathbf{S}})$ is the approximate hessian of Sorella's stochastic reconfiguration with approximate hessian (SRH) method (which converges more slowly than our linear and Newton methods). The present method provides an automatic stabilization of the SRH method by a positive definite matrix $-\Delta E\bar{\mathbf{S}}$ making the hessian nonnegative definite.

Stabilization

If far from the minimum, or, N_{MC} , is small, then the Hessian, \bar{E}_{ij} , need not be positive definite (whereas variance-minimization Levenberg-Marquardt \bar{E}_{ij} is positive definite).

Even for positive definite \bar{E}_{ij} , the new parameter values may make the wave function worse if quadratic approximation is not good.

Add a_{diag} to the diagonal elements of the Hessian. This shifts the eigenvalues by the added constant. As a_{diag} is increased, the proposed parameter changes become smaller and rotate from the Newtonian direction to the steepest descent direction, but in practice a_{diag} is tiny.

The linear method and the perturbative method can be approximately recast into the Newton method. Consequently we can use the same idea for the linear and perturbative methods too.

Stabilization with Correlated Sampling

Each method has a parameter a_{diag} that automatically adjusts to make the method totally stable:

1. Do a MC run to compute the gradient and the Hessian (or overlap and Hamiltonian).
2. Using the above gradient and Hessian (or overlap and Hamiltonian), use 3 different values of a_{diag} to predict 3 different sets of updated parameters.
3. Do a short correlated sampling run for the 3 different wave functions to compute the energy differences for the 3 wave functions more accurately than the energies themselves.
4. Fit a parabola through the 3 energies to find the optimal a_{diag} .
5. Use this optimal a_{diag} to predict a new wave function, using the gradient and Hessian computed in step 1.
6. Loop back

Comparison of Newton, linear and perturbative methods

Programming effort and cost per iteration:

1. Newton method requires ψ , ψ_i , ψ_{ij} , $\hat{H}\psi$, $\hat{H}\psi_i$. ($\hat{H}\psi_{ij}$ removed by Hermiticity)
2. Linear method requires ψ , ψ_i , $\hat{H}\psi$, $\hat{H}\psi_i$.
3. Perturbative method requires ψ , ψ_i , $\hat{H}\psi$, $\hat{H}\psi_i$.
Perturbative method with approx. denom., and, SR require ψ , ψ_i , $\hat{H}\psi$.

Convergence with number of iterations:

1. Newton and linear methods converge in 2-10 iterations for all parameters (CSF, orbital and Jastrow), but sometimes orbitals and exponents can take much longer.
2. Perturbative method converges in 2-10 iterations for CSF and orbital parameters but is very slow for Jastrow because eigenvalues of Hessian for Jastrow span 10-12 orders of magnitude. (Perturbative method can be viewed as Newton with crude Hessian.)

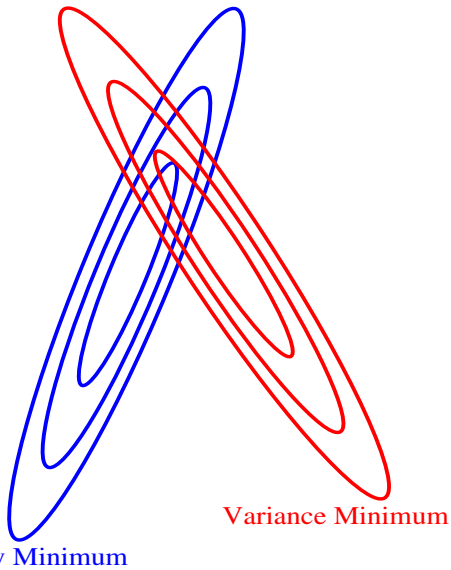
Things to note

Eigenvalues of \bar{E}_{ij} for Jastrow parameters typically span 10-12 orders of magnitude. So steepest descent would be horribly slow to converge!

Take Home Message:

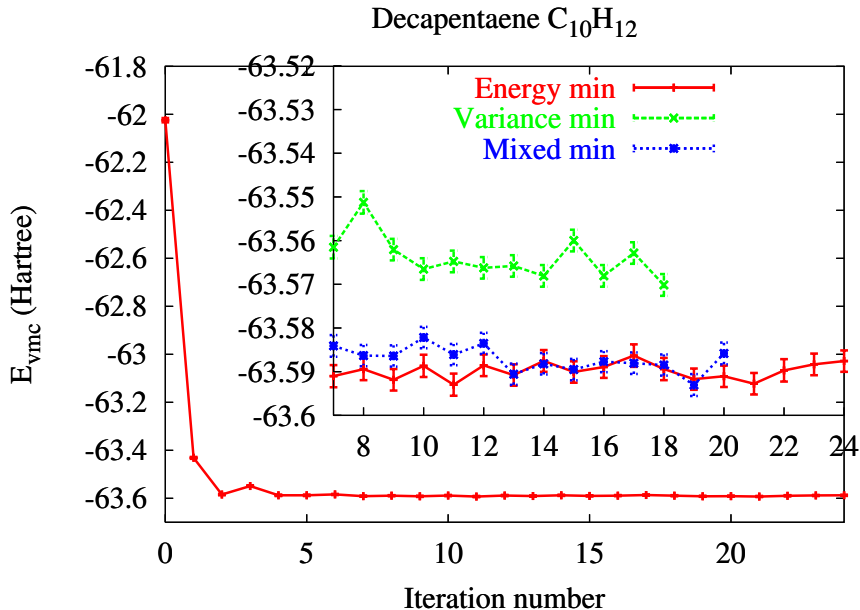
Any method that attempts to minimize the energy, by minimizing the energy evaluated on a set of MC points, will require a very large sample and be inefficient.
Each of the 3 methods presented above avoids doing this.

Optimization of linear combination of energy and variance

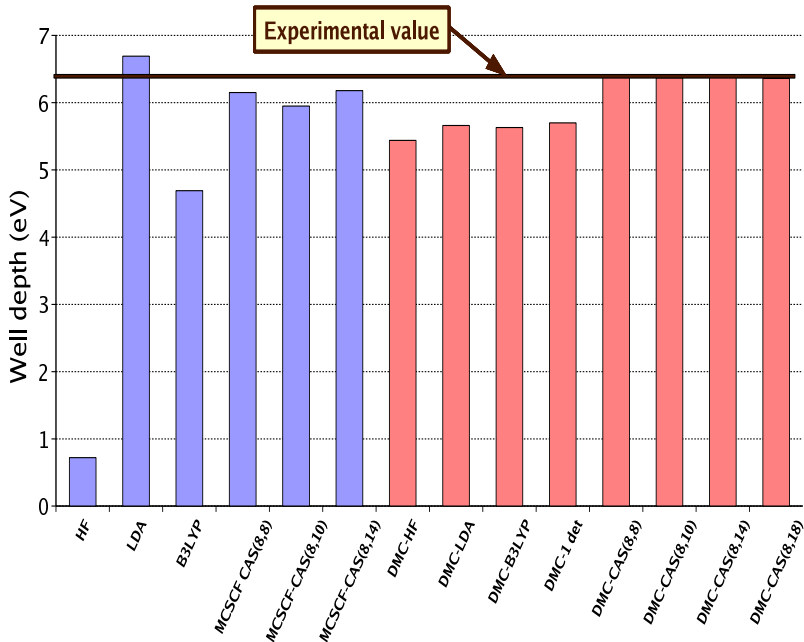


1. Can reduce the variance, without sacrificing appreciably the energy, by minimizing a linear combination, particularly since the ratio of hard to soft directions is 11 orders of magnitude.
2. Easy to do – obvious for Newton. Not obvious, but easy to do for linear method as shown above.
3. Measure of efficiency of the wave function is $\sigma^2 T_{\text{corr}}$.

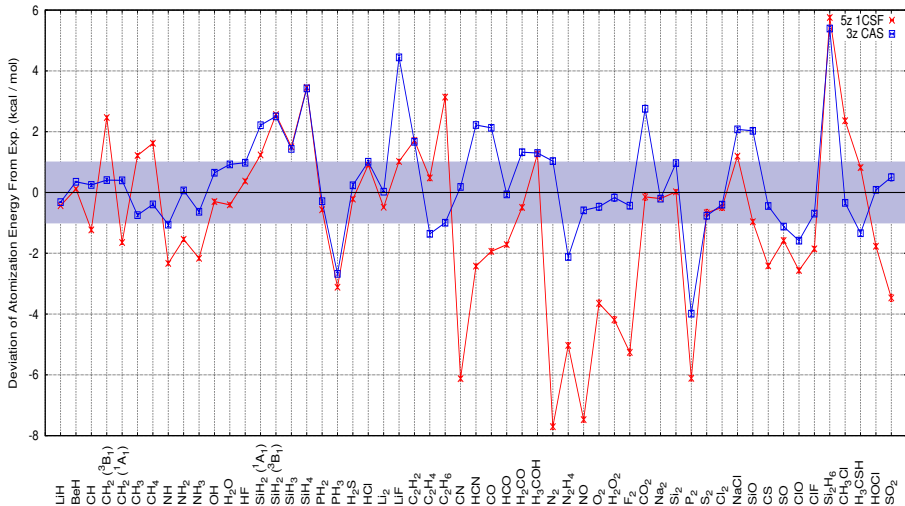
Convergence of energy of decapentaene $C_{10}H_{12}$



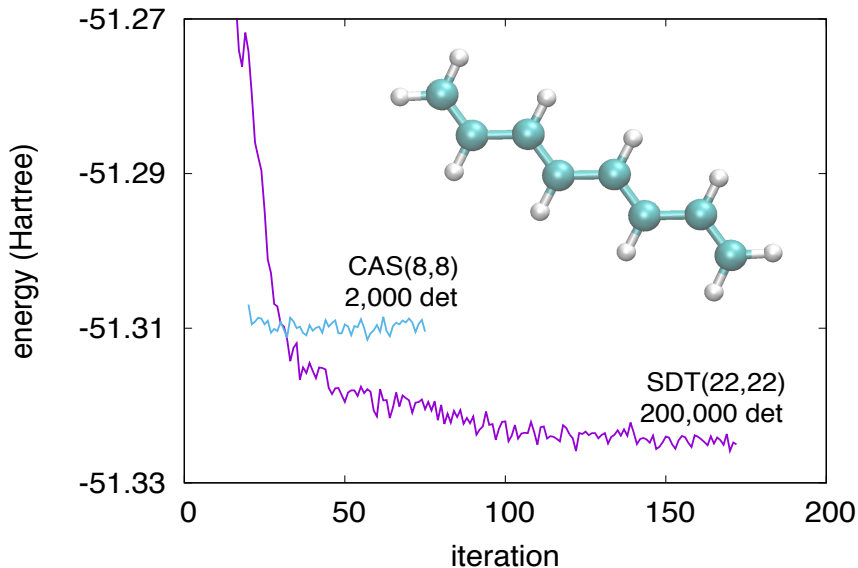
Well-depth of C₂



Atomization energies of the G2 set



The mean absolute deviation from experiment for the DMC energies using the FV-CAS trial wave functions is 1.2 kcal/mole. [Petruzielo, Toulouse, CJU, JCP 2012](#)



Optimization of wavefunction and geometry of C_8H_{10} (42 electrons) with 201924 determinants (all SDT in a space of 22 electrons in 22 orbitals) and 58652 parameters. 10 hours on 128 cores. [Filippi, Assaraf, Moroni, arXiv 2017](#)