

QMC Summer School 2025

Introduction to Quantum Monte Carlo

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https://github.com/QMCPACK/qmc_summer_school_2025

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Outline

The electronic structure problem

Variational solutions and Variational Monte Carlo

Wavefunction optimization

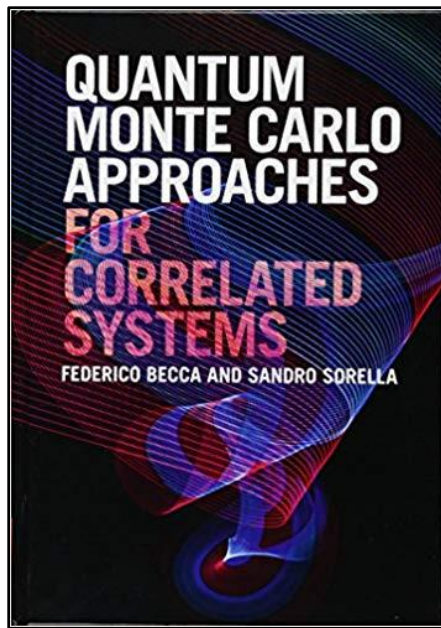
Diffusion Monte Carlo

Practicalities

Next session: Pseudopotentials, Workflows and Statistical Analysis

Where to find more information

Quantum Monte Carlo simulations of solids	
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R. J. Needs and G. Rajagopal TCM Group, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom	
(Published 5 January 2001)	
This article describes the variational and fixed-node diffusion quantum Monte Carlo methods and how they may be used to calculate the properties of many-electron systems. These stochastic wavefunction-based approaches provide a very direct treatment of quantum many-body effects and are as benchmark against which other techniques may be compared. They complement the first-principles density-functional approach by providing more accurate results and a deeper understanding of the physics of electronic correlation in real materials. The algorithms are particularly powerful in correctly estimating high-performance computer-allowable approximations to the ground-state energy of many-electron systems. With these tools one can study computational problems such as the properties of carbon and defects, including dislocation cores, with high precision. The authors provide a pedagogical overview of the techniques and discuss a selection of applications to ground and excited states of solids and clusters.	
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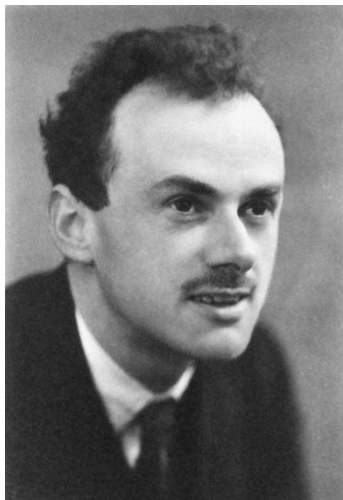


CHEMICAL REVIEWS	
Noncovalent Interactions by Quantum Monte Carlo	
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ABSTRACT: Quantum Monte Carlo (QMC) is a family of stochastic methods for solving quantum many-body problems such as the stationary Schrödinger equation. The review introduces basic notions of electronic structure QMC, based on random walks in real space as well as its advances and adaptations to systems with noncovalent interactions. Specific issues such as fixed-node error cancellation, corrections of trial wave functions, and efficiency considerations that allow for benchmark quality QMC energy differences are described in detail. Comprehensive overviews of article topics QMC applications to systems with noncovalent interactions over the last three decades. The current status of QMC with regard to efficiency, applicability, and stability by nonexperts together with further considerations about QMC developments, limitations, and unresolved challenges are discussed as well.	
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1. INTRODUCTION	
Noncovalent interactions are abundant in nature ^{1,2} and are very important in many research areas such as chemistry, ^{3–7} biology, ^{8–10} biotechnology, ^{11–13} molecular recognition, ¹⁴ drug design, ^{15–17} materials science, ^{18,19} and beyond. Due to their technological and fundamental importance, noncovalent interactions are studied very extensively using a broad range of experimental, theoretical, and computational approaches. ^{20–22} In particular, theory and computations are indispensable not only for understanding, interpretation, and validation of experimental measurements but also for obtaining information that is complementary to what is accessible in experiments. ²³ Noncovalent interactions include hydrogen bonds, which combine experiments with theory ²⁴ in order to gain more comprehensive insight and deeper fundamental understanding.	
There are many distinct types of noncovalent interactions that differ in their origin or nature of the interacting species. Hydrogen bonding and stacking (or π - π interactions) are	
Special Issues: Noncovalent Interactions	
Received: September 30, 2015	
Published: April 15, 2016	
ACS Publications	
© 2016 American Chemical Society	
DOI: 10.1021/acschemrev.5b00177	
ACS Chem Rev. 2016, 15, 1188–1215	

Classic, easy-to-read review: W. Foulkes et al, Rev. Mod. Phys. **73** 33 (2001) [no new methods]
M. Dubey et al. Chem Rev. **116** 5188 (2016) [focus on non-covalent interactions]
QMCPACK: P. R. C. Kent et al. J. Chem. Phys. **152** 174105 (2020) and other QMC papers in special issue, J. Kim et al. JPCM **30** 195901 (2018). Code reproducibility: arXiv:2501.12950

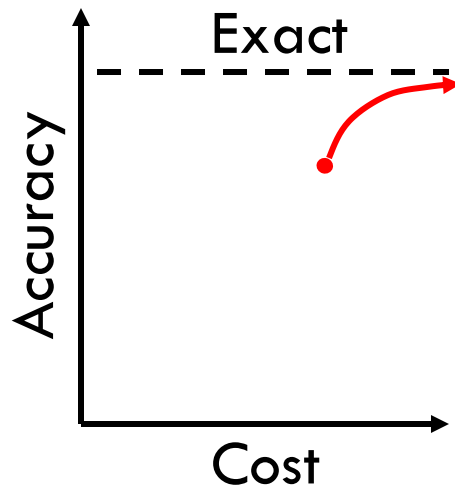
The Electronic Structure Problem

We seek accurate and reliable *ab initio* solutions of the Schrödinger equation for models of real materials and molecules. We need high accuracy methods where any approximations can be made smaller and the methods can be applied to general systems: molecules, insulators, metals, surfaces, interfaces, and nanostructures...



“The underlying physical laws necessary for the mathematic theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that **the exact application of these laws leads to equations much too complicated to be soluble.** It therefore becomes desirable that **approximate practical methods of applying quantum mechanics should be developed...**”

Paul Dirac, Proc. Roy. Soc. (1929)



Solving the Schrödinger Equation

Ideally, we would be able to exactly and cheaply solve the zero temperature Schrödinger equation for general molecular and solid-state systems. We could then obtain their general properties without invoking unknown approximations.

$$\hat{H}\Psi = E_0\Psi$$

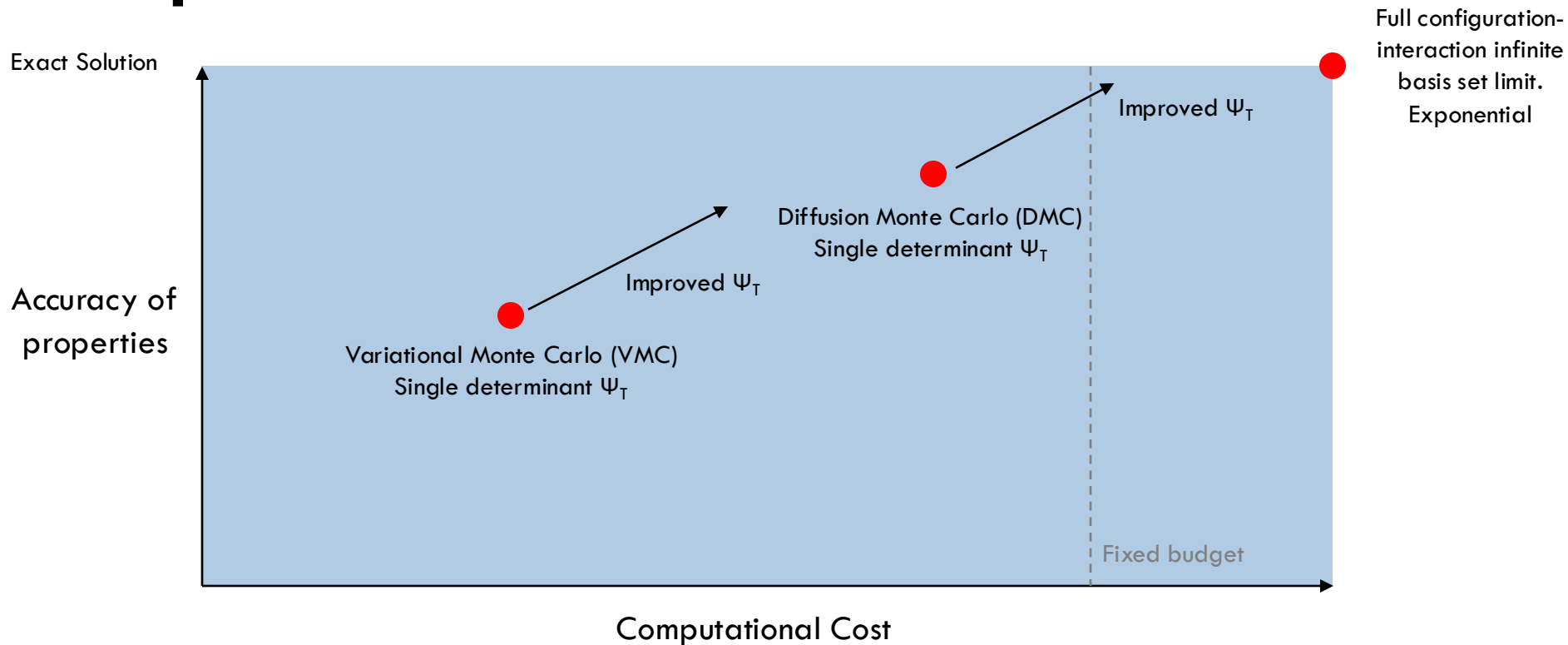
$$\hat{H} = -\frac{1}{2} \sum_i^{N_e} \nabla_i^2 - \sum_i^{N_e} \sum_{\alpha}^{N_{\alpha}} \frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{d}_{\alpha}|} + \sum_i^{N_e} \sum_{j < i}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}) = -\Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_{N_e})$$

Key difficulty: The Fermionic wavefunction must be antisymmetric w.r.t. exchange of any two electrons.

Troyer & Wiese PRL 2005 showed finding exact Fermionic QMC solution to be “non-deterministic polynomial-time hard” – we can’t expect to find a polynomial scaling or non-combinatorial scaling solution that is also exact.

Perspective on QMC Methods



We seek improvable (“pay more, get more”) methods combining accuracy, efficiency, applicability.

Note: Ceperley & Alder PRL 1980 homogeneous electron gas using release node QMC is formally exact but impractically exponentially scaling

Outline

The electronic structure problem

Variational solutions and Variational Monte Carlo

Wavefunction optimization

Diffusion Monte Carlo

Practicalities

Variational Wavefunction Approach

From variational principle, we know the energy of any guessed trial wavefunction \geq ground state energy E_0 .

$$E_T = \frac{\int \Psi_T^* \hat{H} \Psi_T}{\int \Psi_T^* \Psi_T} \geq E_0$$

We will need accurate Ψ_T and methods to further improve them

We could do this numerically, but conventional numerical integration scales with the power of the dimensionality $\sim a^{3N_e}$ - not practical for more than a few electrons. We can avoid the “curse of dimensionality” via Monte Carlo integration:

$$E_T = \int \left(\frac{|\Psi_T|^2}{\int |\Psi_T|^2} \right) \left(\frac{\hat{H} \Psi_T}{\Psi_T} \right) \geq E_0$$

Local energy E_L

Treat $|\Psi_T|^2$ as a probability density function (normalized, continuous, non-negative) and use to importance sample the local energy using the Metropolis algorithm.

Sampling $|\Psi_T|^2$ with Metropolis Monte Carlo

Use the classic Metropolis algorithm (JCP 1953): we always move to more likely locations, sometimes move to less likely locations.

For every step:

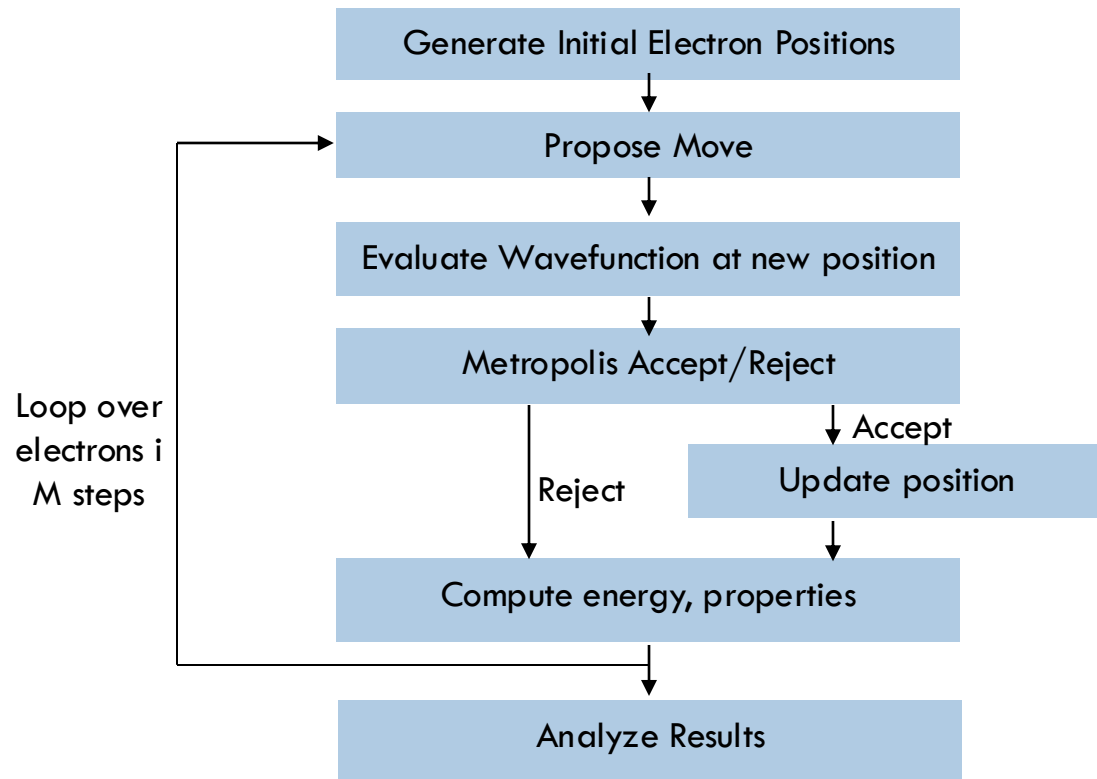
For every electron i :

Propose moving \mathbf{r}_i to \mathbf{r}'_i via probability $T(\mathbf{r}'_i \leftarrow \mathbf{r}_i)$

Accept with probability $A(\mathbf{r}'_i \leftarrow \mathbf{r}_i) = \text{Min} \left(1, \frac{T(\mathbf{r}_i \leftarrow \mathbf{r}'_i)|\Psi_T(\mathbf{r}'_i)|^2}{T(\mathbf{r}'_i \leftarrow \mathbf{r}_i)|\Psi_T(\mathbf{r}_i)|^2} \right)$

In variational Monte Carlo, typically use normally-distributed proposed moves, width proportional to an input “timestep”. With typical τ , acceptance rate might be $\sim 50\%$. Acceptance rate only affects efficiency.

Variational Monte Carlo Algorithm



Key measured properties

$$E_{\text{VMC}} \approx \frac{1}{M} \sum_{m=1}^M E_L(\mathbf{R}_m)$$

\mathbf{R}_m = set of electron positions $\{\mathbf{r}_1 \dots \mathbf{r}_N\}$

$$\frac{\sigma^2}{M} \approx \frac{1}{M(M-1)} \sum_{m=1}^M \left(E_L(\mathbf{R}_m) - \left(\frac{1}{M} \sum_{m=1}^M E_L(\mathbf{R}_m) \right) \right)^2$$

Variance σ^2 : measure of width of energy distribution.

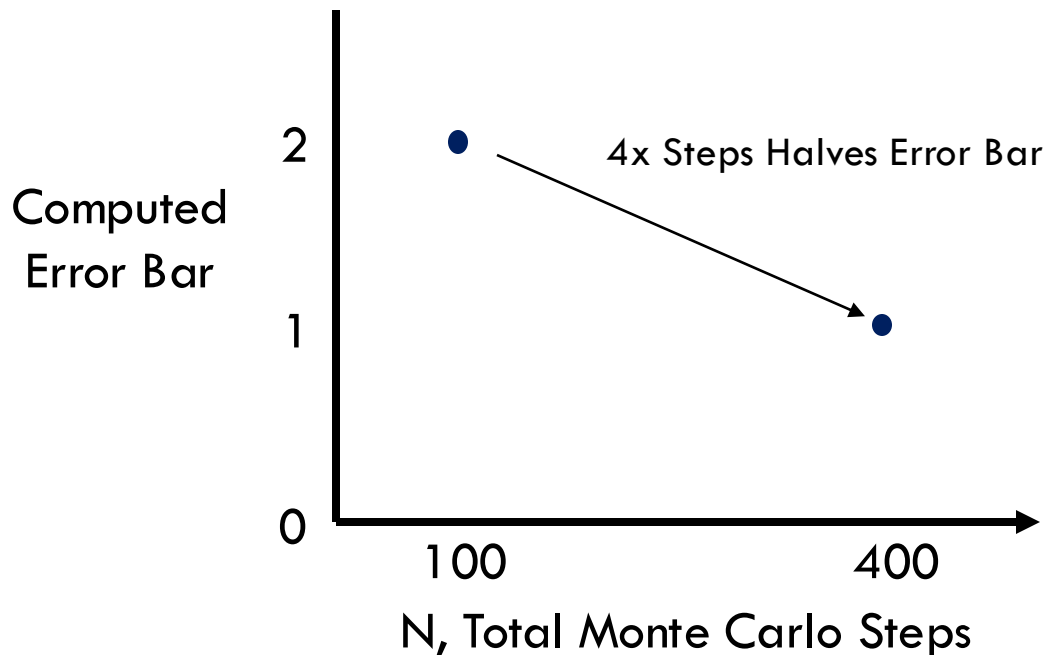
We report $E_{\text{VMC}} \pm \sigma/\sqrt{M}$

Energy and uncertainty in its value.

Assumes the M samples are statistically independent.

Monte Carlo Convergence

Monte Carlo error bar converges as $M^{-0.5}$, M =number of Monte Carlo samples (or steps, time). We can use this to project costs and verify statistical analysis. Statistical convergence is independent of dimensionality.



$$\text{Standard error of mean} \propto \frac{1}{\sqrt{M}}$$

Error bar should halve if we run 4x longer. Reducing by 10x will cost 100x in run time. Thoughtful planning essential.

Trial Wavefunctions

Start with the best available mean-field or correlated wavefunction, improve via Jastrow factor and (re)optimization of coefficients/parameters $\{\mathbf{p}\}$. Jastrow factor improves accuracy over HF determinant or CI expansion alone.

$$\Psi_T = (D_0 + \sum_{ab} c_a^b D_a^b + \sum_{abcd} c_{ab}^{cd} D_{ab}^{cd} + \dots) \exp(J(r_{ij}, r_{il}, r_{ijl}, \dots))$$



Starting point for solids: Single determinant D_0 of orbitals from DFT (HSE06, PBE0, DFT+U, SCAN, PBE). Single determinant has required Fermionic symmetries.

Starting point for molecules: Single determinant D_0 of orbitals from DFT (HSE06, PBE0, DFT+U, SCAN, PBE) or HF.

Advanced molecules: Multideterminant expansion from CISD, CASSCF, ... optimize expansion coefficients. (Full CI is already a convergent wavefunction representation)

State of the art: Full reoptimization of orbitals in determinants and multideterminant expansion coefficients.



Parameterized **Jastrow factor**. **Build in physics & electron correlations directly**. e.g. wavefunction cusps, shape near electron coalescence. *Greatly* improves trial wavefunction. Does not change nodes. 1, 2, 3-body terms with some cutoff.

$$J(\{\mathbf{r}_i\}, \{\mathbf{r}_I\}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N u(r_{ij}) + \sum_{I=1}^{N_{\text{ions}}} \sum_{i=1}^N \chi_I(r_{iI})$$

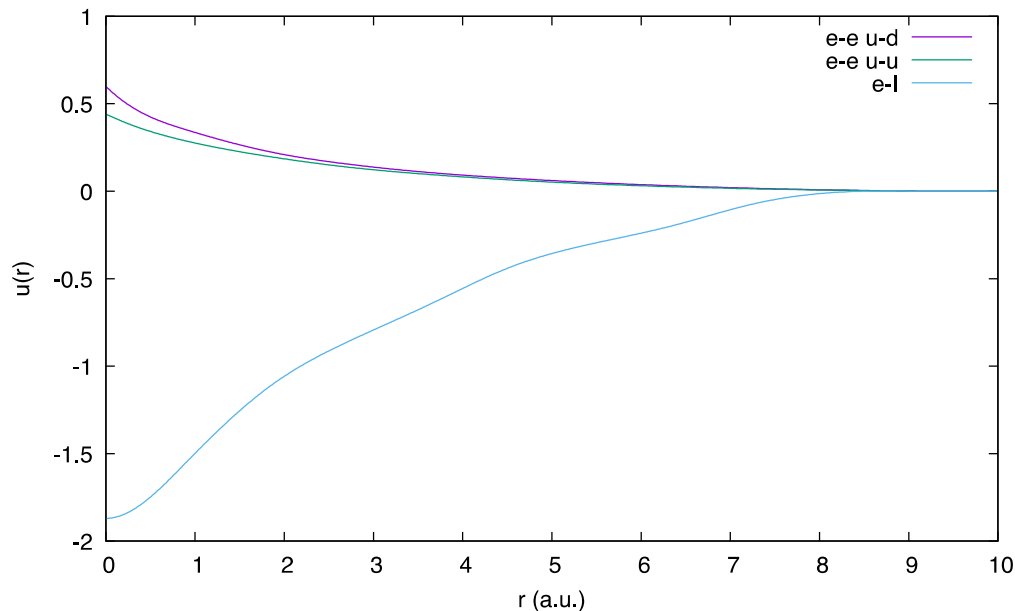
$$+ \sum_{I=1}^{N_{\text{ions}}} \sum_{i=1}^{N-1} \sum_{j=i+1}^N f_I(r_{iI}, r_{jI}, r_{ij}) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N p(\mathbf{r}_{ij})$$

$$+ \sum_{i=1}^N q(\mathbf{r}_i), \quad \text{Drummond et al. PRB } \mathbf{70} \text{ 235119 (2004)}$$

Example Jastrow Factors

The standard efficient choice in QMCPACK is to represent the two-body (electron-electron) and one-body (electron-ion) terms via numerical splines, interpolated through a chosen number of points. The values of the splines at these points are optimized.

e-e part is always spin-polarized to account for different cusp conditions.



Jastrow components
for all-electron C_{24}

In this example 10 points
were used for each
component (30 parameters)
along with a 10 a.u. cutoff

Stochastic Wavefunction Optimization

Given a parameterized trial wavefunction $\Psi_T(\mathbf{p}, \mathbf{R})$ we need to find the optimal parameters \mathbf{p} that give the “best” wavefunction

Properties to exploit:

$$E_T = \frac{\int \Psi_T^* \hat{H} \Psi_T}{\int \Psi_T^* \Psi_T} \geq E_0$$

$$\frac{\sigma^2}{M} \approx \frac{1}{M(M-1)} \sum_{m=1}^M \left(E_L(\mathbf{R}_m) - \left(\frac{1}{M} \sum_{m=1}^M E_L(\mathbf{R}_m) \right) \right)^2$$

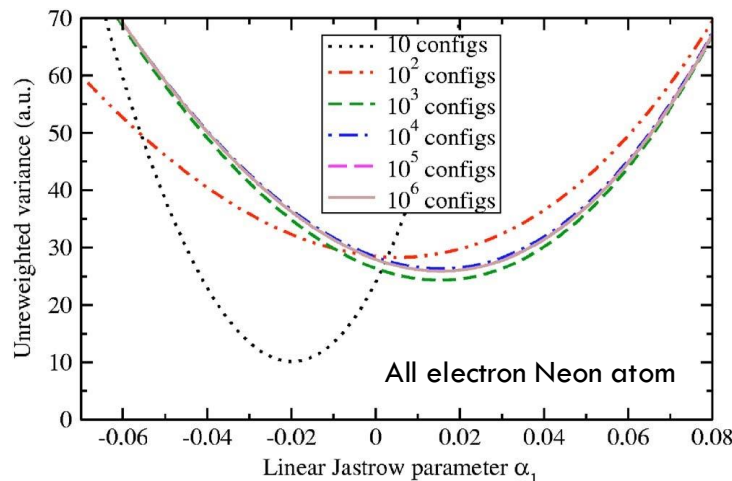
$$\sigma^2 \geq 0$$

Via the variational principle lower energies are better, & when $\Psi_T = \Psi_0$ we obtain the ground state energy $E_T = E_0$. The variance σ^2 also decreases and is zero for exact eigenstates. Gives a measure of wavefunction quality without knowing the exact ground state energy.

Variance Minimization

Use a Newton-like optimizer to minimize the variance of a set of configurations from VMC by optimizing \mathbf{p} . Obtain $E(\mathbf{p}')$ by reweighting probabilities for new $\Psi_T(\mathbf{p}')$ to obtain correct statistics and recalculate energies efficiently. Repeat multiple times with fresh VMC configurations to allow for large changes.

$$\left| \frac{\Psi(\mathbf{p}')}{\Psi(\mathbf{p})} \right|^2$$



“Efficient scheme for optimizing linear Jastrow factors”
Drummond & Needs PRB **72** 085124 (2005)

Even for Ne atom, needed >1000
configurations in optimization

In practice, variance minimization doesn't give greatest accuracy for complex trial wavefunctions, but remains a good way to get an initial trial for use in other algorithms. Many other methods historically proposed, e.g. different numerical optimization methods, via finding optimized potential for single particle orbitals, maximizing overlap with DMC configurations...

Linear Method / “Energy Minimization”

In 2007, Umrigar and coworkers showed how to make practical VMC energy optimization for **non-linear and linear parameters** via a linear-order expansion of the wavefunction & a **stabilized diagonalization** of subsequent Schrodinger-like equation. Now the standard method and capable of optimizing all parameters in trial wavefunctions. Snags: Can be brittle; higher memory use.

$$\Psi_{lin}(\mathbf{p}, \mathbf{R}) = \Psi_0(\mathbf{p}_0, \mathbf{R}) + \sum_{i=1}^{N_{opt}} \Delta p_i \left(\frac{\partial \Psi(\mathbf{p}, \mathbf{R})}{\partial p_i} \right)_{\mathbf{p}=\mathbf{p}_0}$$

$$\mathbf{H} \Delta \mathbf{p} = \mathbf{E} \mathbf{S} \Delta \mathbf{p},$$

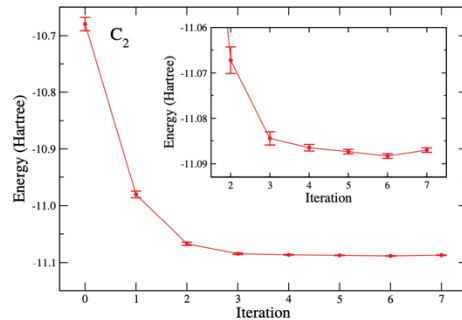
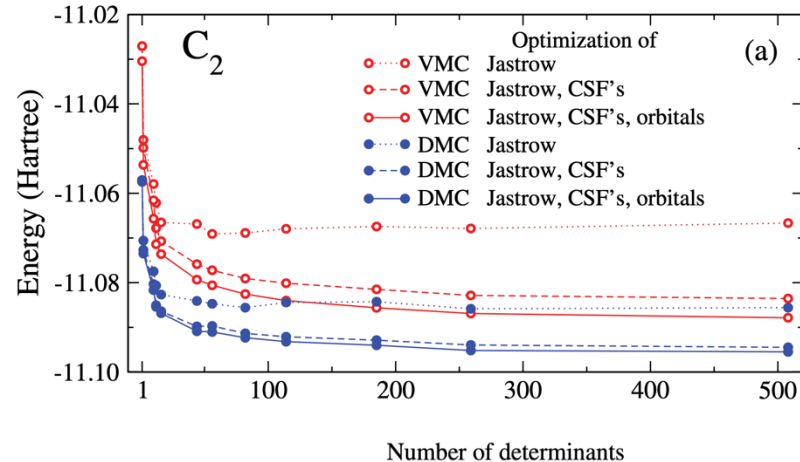


FIG. 1 (color online). Convergence of the VMC total energy of the C_2 molecule when simultaneously optimizing 24 Jastrow, 73 CSF and 174 orbital parameters for a truncated CAS(8,14) wave function. The number of MC configurations range from 10000 for the first iteration to 400000 for the last iterations.



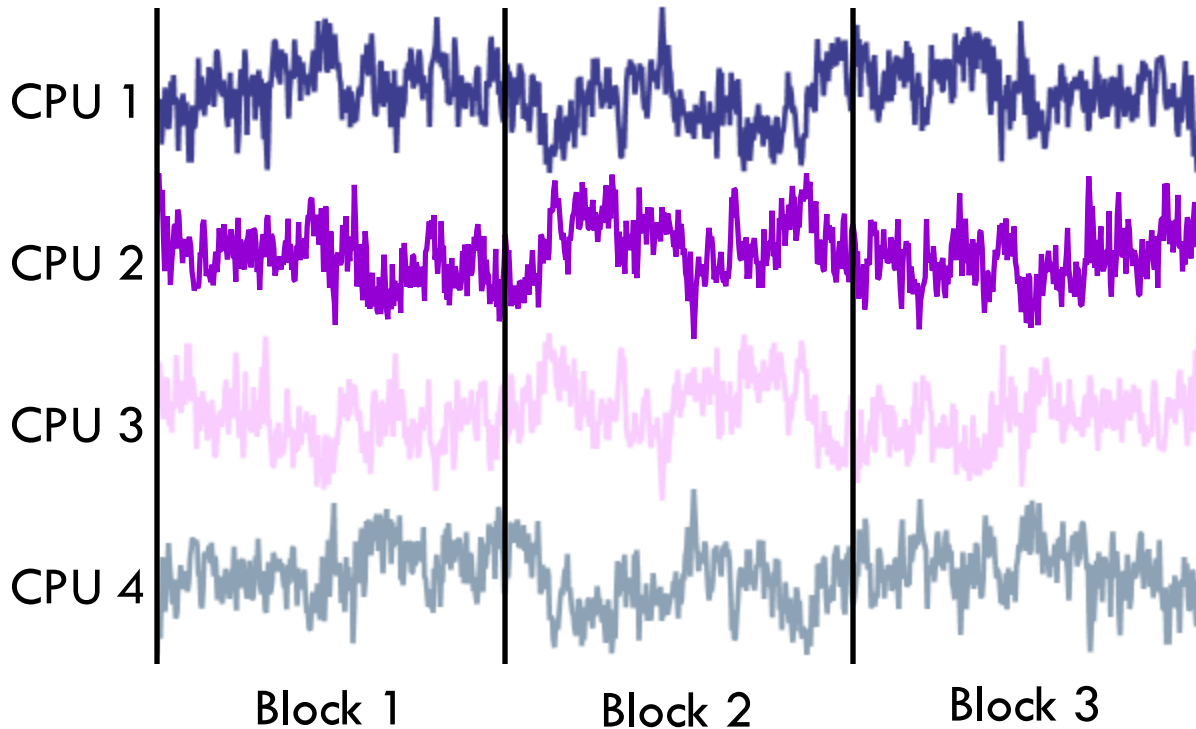
“Alleviation of the Fermion sign problem by optimization of many-body wavefunctions”

C. J. Umrigar et al. PRL **98** 110201 (2007)

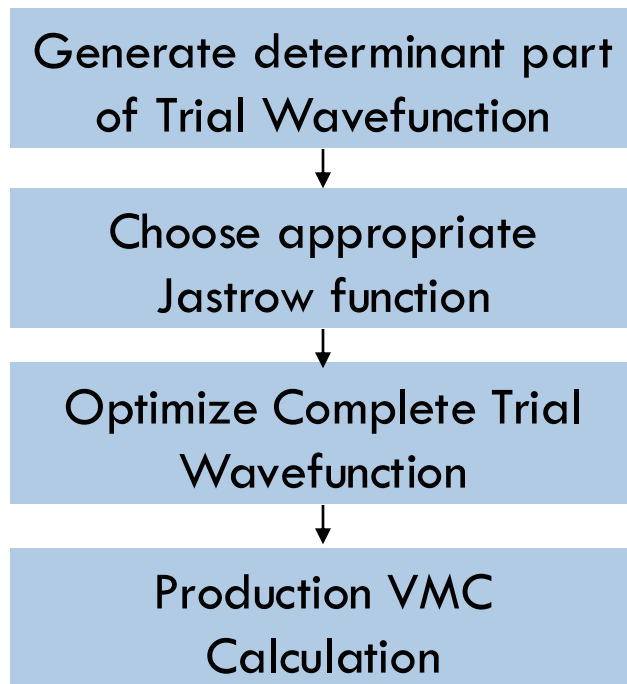
Mapping VMC to computers

Simply put one independent “walker”/Markov chain on each CPU core

Subdivide run in “blocks” and write out summary statistical results every block for convenience.



VMC workflow



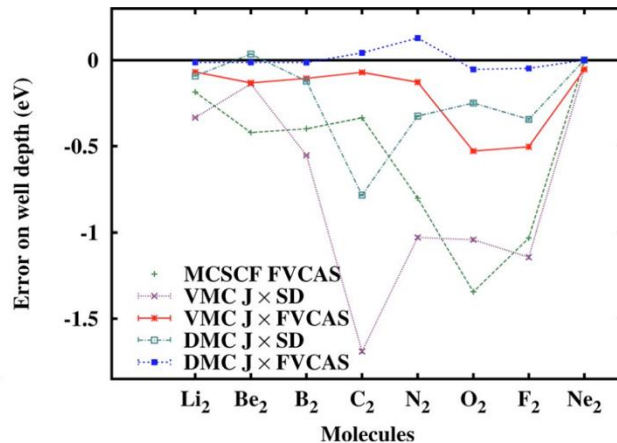
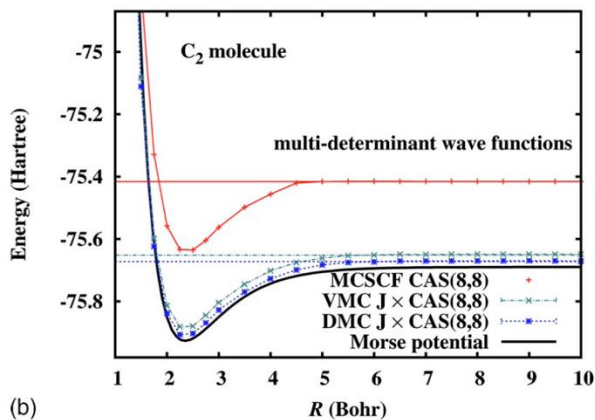
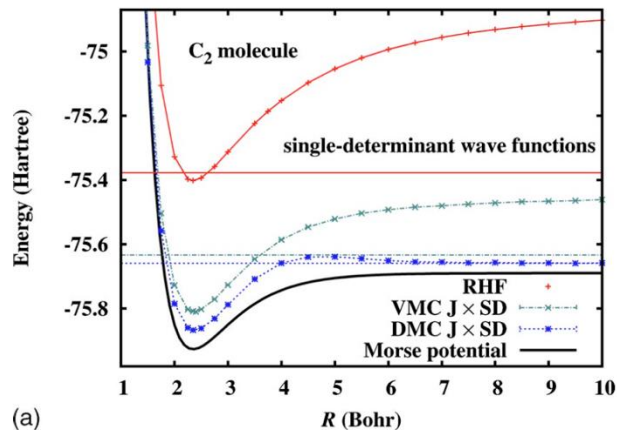
← Large basis set DFT, HF, CASSCF, CI calculation using standard code. Standard recipe: single determinant

← Commonly just the Jastrow part, increasingly determinant and orbital coefficients as well

1st application: optimize timestep, try different Jastrow functions

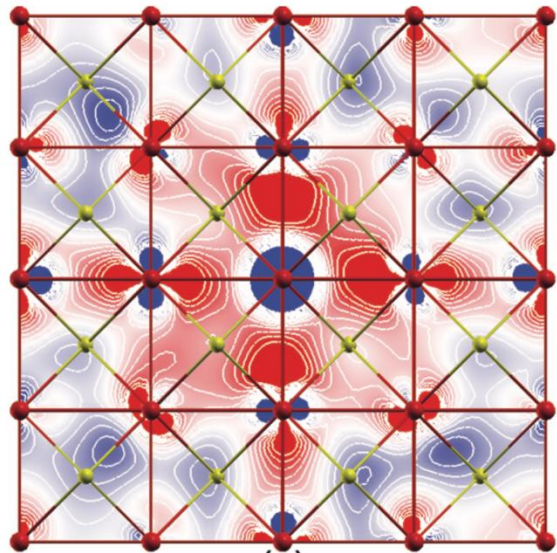
Example VMC Calculations

First row atoms and diatomic molecules from Toulouse & Umrigar JCP **128** 174101 (2008)



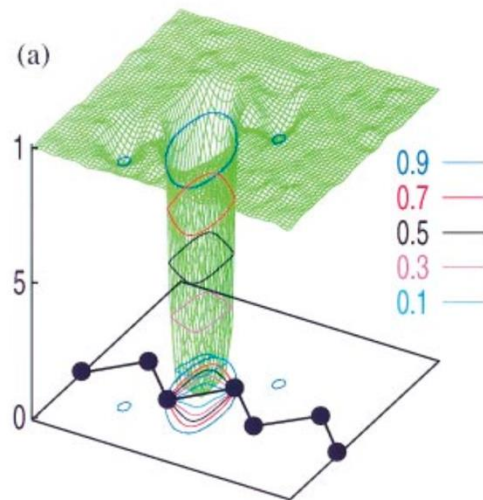
Example VMC Calculations (advanced!)

Exploiting flexibility to integrate over trial wavefunction or input novel pairing trial wavefunction



Pairing function in FeSe Superconductors

Up to 10K independent parameters, 352 electrons
Casula & Sorella PRB **88** 155125 (2013)



$$\bar{g}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \frac{N(N-1)}{n_{\alpha}(\mathbf{r})n_{\beta}(\mathbf{r}')} \int_0^1 d\lambda \int d\mathbf{x}_3 \cdots d\mathbf{x}_N \times |\Psi_{\lambda}(\mathbf{r}\alpha, \mathbf{r}'\beta, \mathbf{x}_3, \dots, \mathbf{x}_N)|^2, \quad (4)$$

$g(\mathbf{r}, \mathbf{r}')$ in bulk silicon. R. Q. Hood et al.
PRL **78** 3350 (1997)

Key features of VMC

Advantages

Explicit form of trial wavefunction

- Can use any trial wavefunction we can imagine, motivated by physics/chemistry, not ease of integration.
- Can directly compute any observable.
- Simple Monte Carlo – no timestep error or other discretization introduced.
- Nominally cubic scaling with system size.

Disadvantages

Explicit form of trial wavefunction

- Limited to forms of trial wavefunction we can imagine - high accuracy difficult for solids, correlated physics, may not have consistent errors.
- Potentially many parameters to optimize reliably. Not yet automated/“push button”.

All QMC methods: Need to perform finite size scaling even for bulk materials in periodic calculations.

Questions?

Break

Outline

The electronic structure problem

Variational solutions and Variational Monte Carlo

Wavefunction optimization

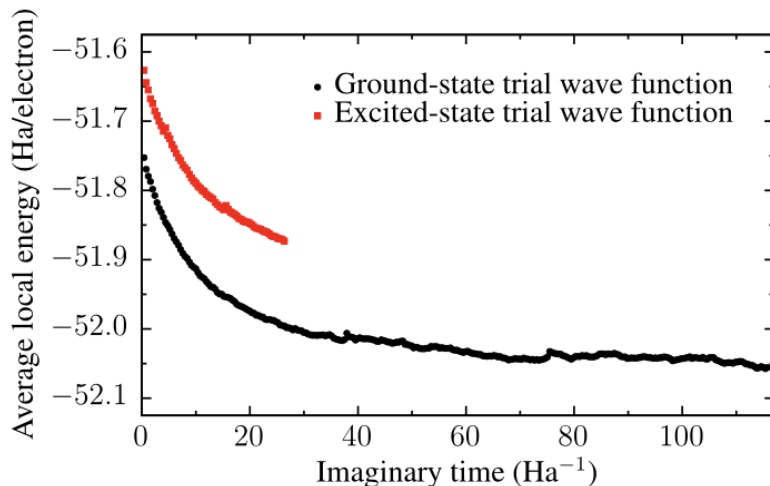
Diffusion Monte Carlo

Practicalities

Diffusion Quantum Monte Carlo

Projector Quantum Monte Carlo methods, such as DMC, are based on the time-dependent evolution of wavefunctions and the imaginary time Schrodinger equation. At long τ excited states drop out. Gives a **systematic improvement** over an approximate input trial wavefunction.

$$\frac{\partial |\psi\rangle}{\partial \tau} = -\hat{H}|\psi\rangle \quad |\psi(\delta\tau)\rangle = \sum_{i=0}^{\infty} c_i e^{-\epsilon_i \delta\tau} |\phi_i\rangle$$



2D HEG, 610 electrons

R. J. Needs et al. JCP **152** 154106 (2020)

Diffusion Quantum Monte Carlo

Derivation is lengthy! Notably, in the importance sampled version we solve for

$$f(\mathbf{R}, t) = \Phi(\mathbf{R}, t) \Psi_T(\mathbf{R})$$

Not $|\Phi|^2$!!!

$$f(\mathbf{R}, t) = \left\langle \sum_{\alpha}^{N_{\text{walkers}}} w_{\alpha} \delta(\mathbf{R} - \mathbf{R}_{\alpha}) \right\rangle$$

Ensemble of
walkers

$$-\frac{\partial f(\mathbf{R}, t)}{\partial t} = -\frac{1}{2} \nabla^2 f(\mathbf{R}, t) + \nabla \cdot [\nabla \ln |\psi_T(\mathbf{R})| f(\mathbf{R}, t)] + \left[\frac{\hat{H} \psi_T(\mathbf{R})}{\psi_T(\mathbf{R})} - E_{\text{ref}} \right] f(\mathbf{R}, t)$$

Walkers drift,
diffuse &
renormalize

Maps well to an existing VMC code with variable population of walkers. **Due**
to Trotter discretization, accuracy is $O(\tau^2)$. Typical acceptance >99%.

See W. M. C. Foulkes RMP 2001,
R. J. Needs JCP 2020 (etc.)

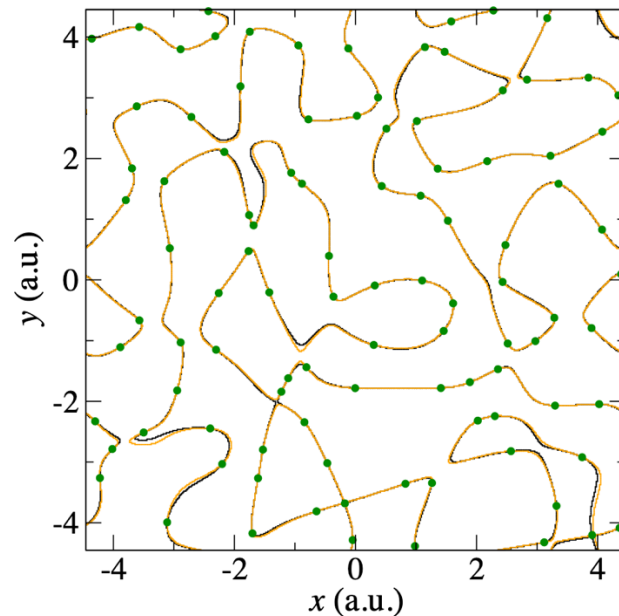
Fixed Node Approximation

To ensure a Fermionic solution we impose that

$$\Phi(\mathbf{R}, t) \Psi_T(\mathbf{R}) \geq 0$$

i.e. we reject moves that would cause the wavefunction to change sign/cross nodes. If not done we would obtain a bosonic solution. This introduces a **variational error in the energy**.

The “tiling theorem” states that the exact ground state can only have one type of nodal pocket. Practically this means this means the same result is obtained independent of starting configurations.



Nodes of 2D HEG $r_s=0.5$ when moving 1 of 101 like spin electrons (green).
Lopez Rios et al. PRE **74** 066701 (2006)

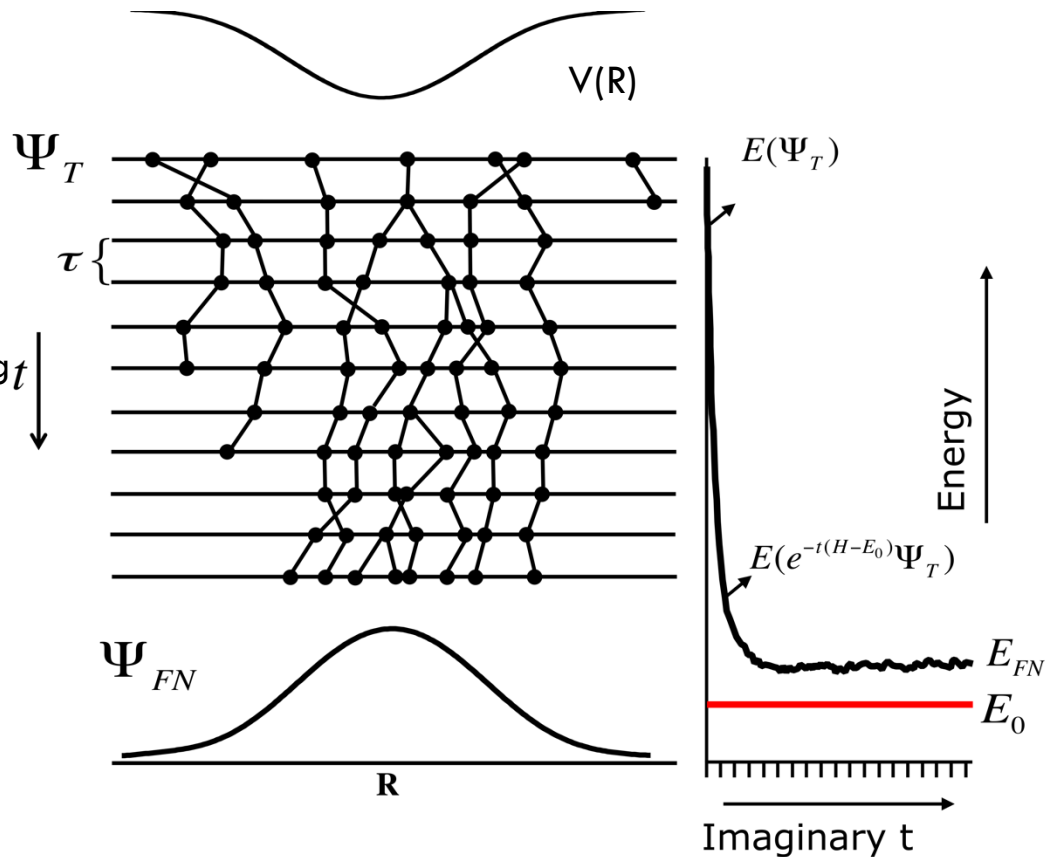
DMC In Practice

DMC algorithm maps onto a time varying population of walkers where walkers in energetically favorable locations multiply and walkers in unfavorable locations are removed. (Can use weights equivalently).

After initial projection to ground state, branching random walk has greatest density where wavefunction probability is largest.

Nodes determine final energy, overall trial wavefunction influences efficiency and timestep error.

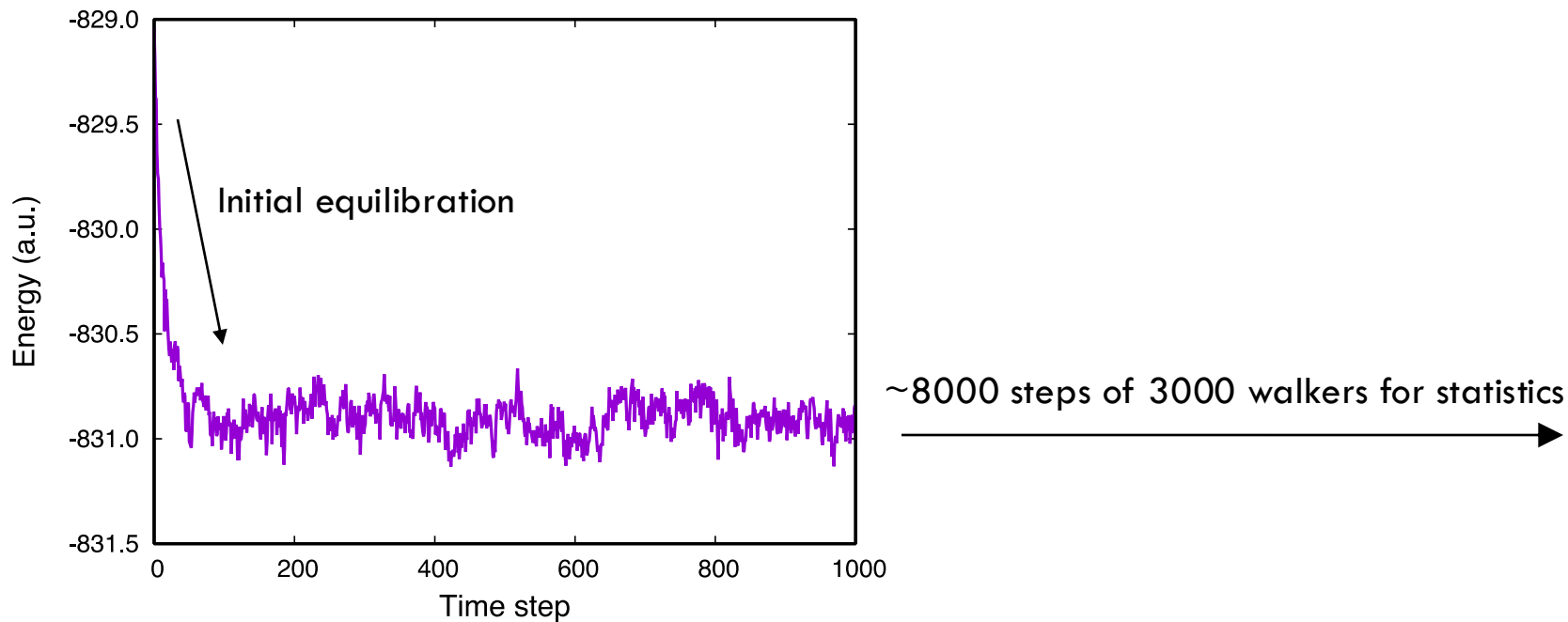
(Not shown) Reference energy is updated smoothly to keep population near target value.



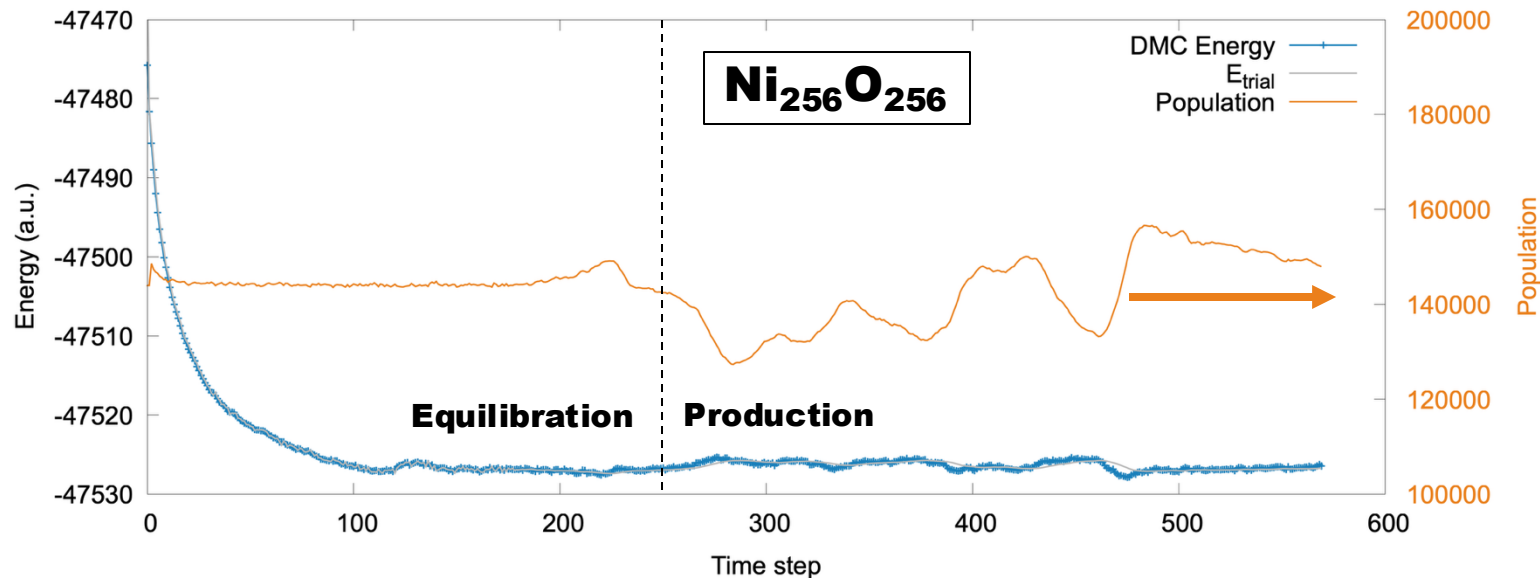
Real-world DMC: 48 atoms, bulk VO_2

Given an input trial wavefunction (and its nodal surface), time-step, and population size we can run DMC

Production run from Kylanpää et al. PRM **1** 065408 (2017). 200 electrons, 0.01 a.u. timestep, wavefunction from DFT+U (U varied to minimize DMC energy).



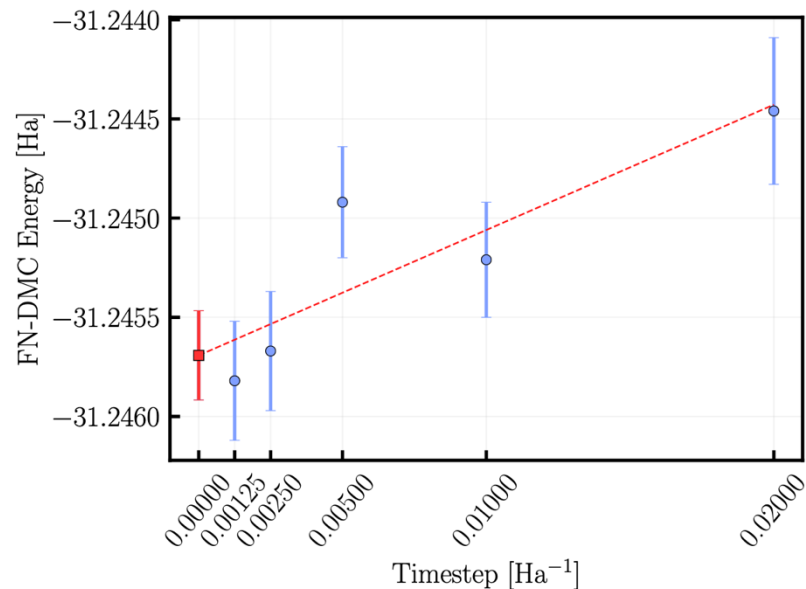
Real-world DMC: 512 atoms, bulk NiO



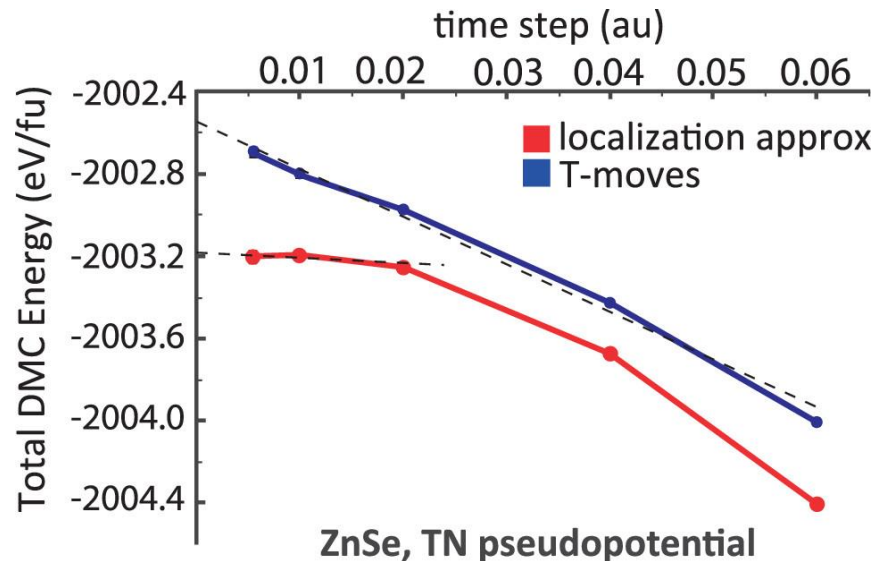
- $\text{Ni}_{256}\text{O}_{256}$ supercell, 6144 total electrons. 0.01 a.u. timestep. Det+J1+J2 (only).
- 0.01 eV/primitive cell final statistical error in ~1h using 9000 nodes/96% of machine.
- Run displays healthy & expected numerical behavior.
- Note: equilibration is a significant fraction of the run. Not optimized for throughput.

Time Step Errors

Properties should be extrapolated to zero time step or a sufficiently small time step chosen that the errors are sufficiently small. Error behavior is transferable to similar systems, e.g. a different isomer.



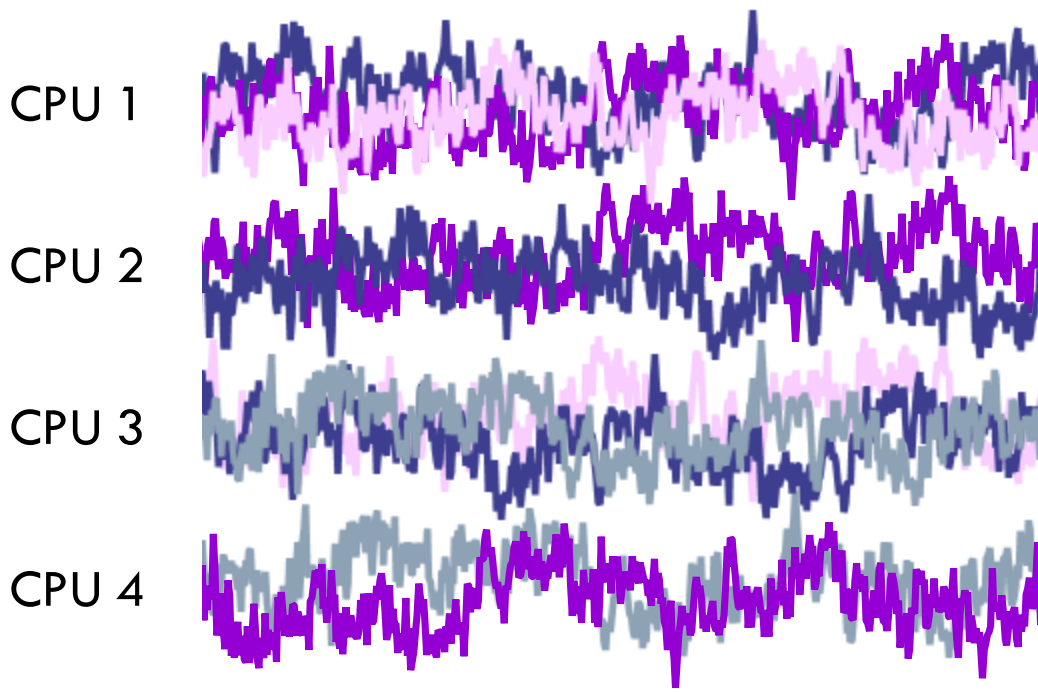
“Bulk silicon benchmarks and systematic control of biases”. Annaberdiyev et al. PRB **103** 205206 (2021)



“Towards a systematic assessment of errors in DMC calculations of semiconductors: ZnSe and ZnO” Yu et al. JCP **143** 224707 (2015)

Mapping DMC to computers

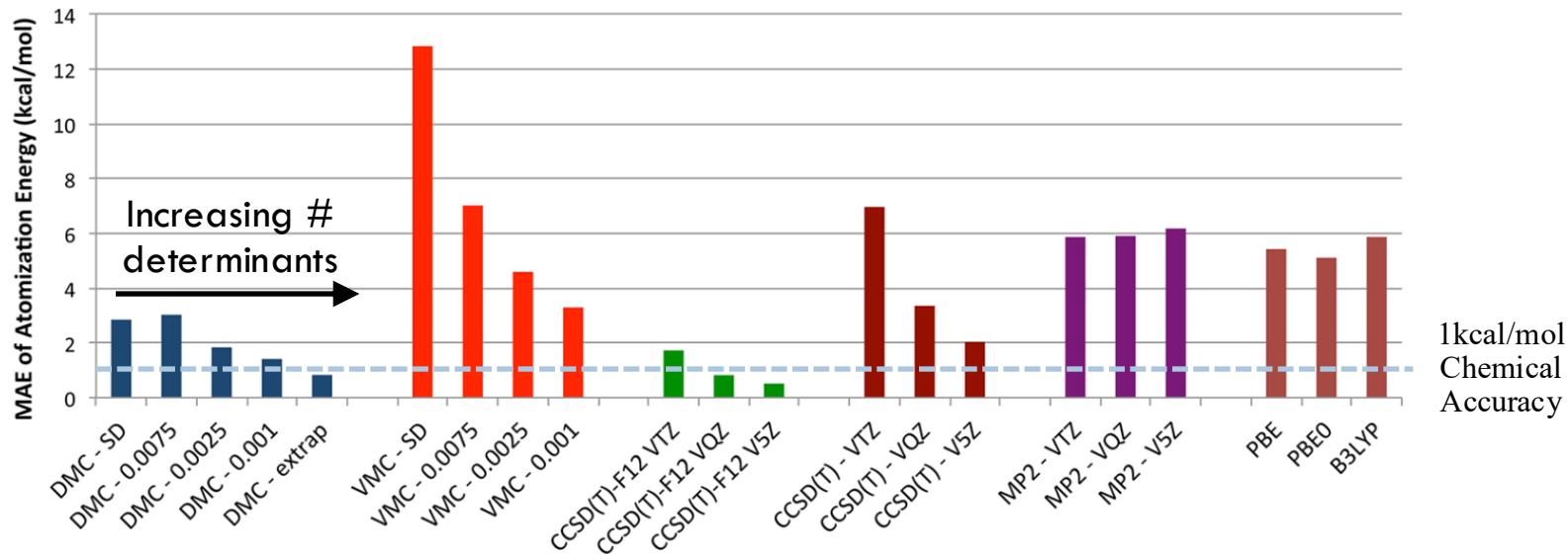
Put many “walkers”/Markov chains on each CPU core or GPU. Overall average energy needed for population control/normalization is updated \sim every step. Write out average energies each step. Many implementations vary overall population of walkers, resulting in load imbalance. Large population helps minimize imbalance.



Example DMC & VMC for Molecular Calculations

Chemical accuracy $< 1 \text{ kcal/mol}$ achieved via the “linear method” for wf optimization.

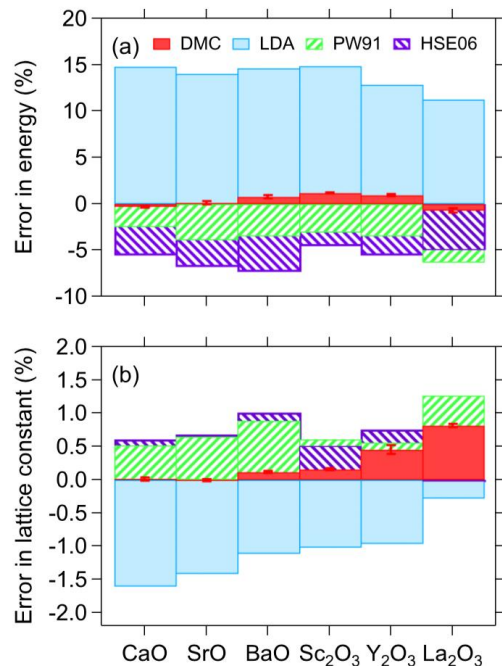
Trial wavefunctions use large multideterminant expansions. DMC better than VMC.



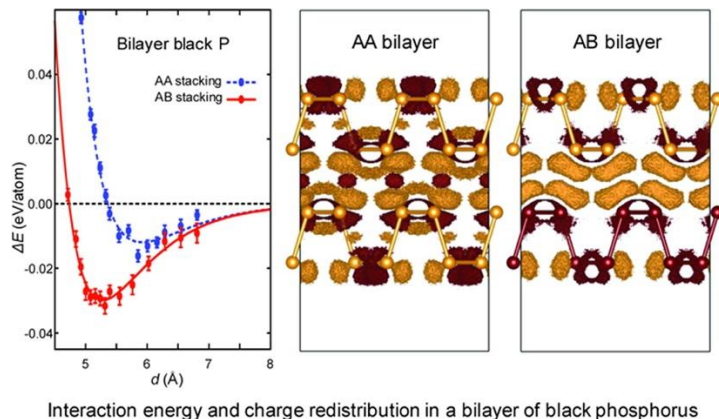
G1 test set. Morales et al. JCTC **8** 2181 (2012)

Example DMC Calculations

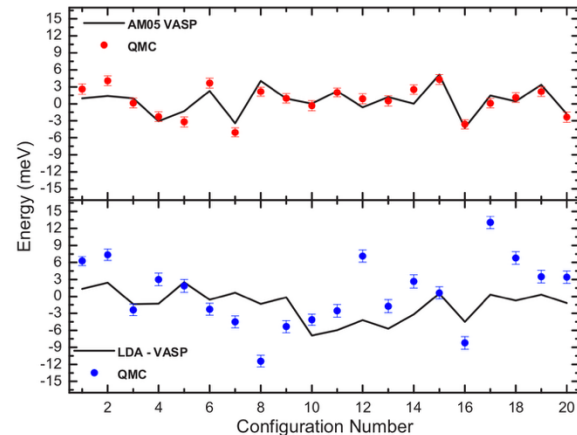
Single determinant DMC calculations for metal oxides. Santana et al. JCP (2016,2017)



Nature of the interlayer interaction in few layer phosphorene. Shulenburg et al. Nano Letters (2015)



Kr liquid at high pressure: AM05 functional found to have best agreement with DMC. Mattsson et al. PRB (2014)



Key features of DMC

Advantages

Gives very accurate and robust results, even with simple nodal surfaces/trial wavefunctions.

Improvable with better quality trial wavefunctions.

Easily takes advantages of supercomputers.

Disadvantages

Unlike VMC, no explicit wavefunction obtained. Mixed estimator problem for non-commuting observables.

Significantly more expensive than VMC.

Small timestep needed for high Z elements.

Finite size scaling & cost in solid-state (Supercells).

Errors, Approximations

“Fixed node” variational error in energy is key approximation.

Timestep error should be tested and converged.

Non-local pseudopotentials need special treatment.

Outline

The electronic structure problem

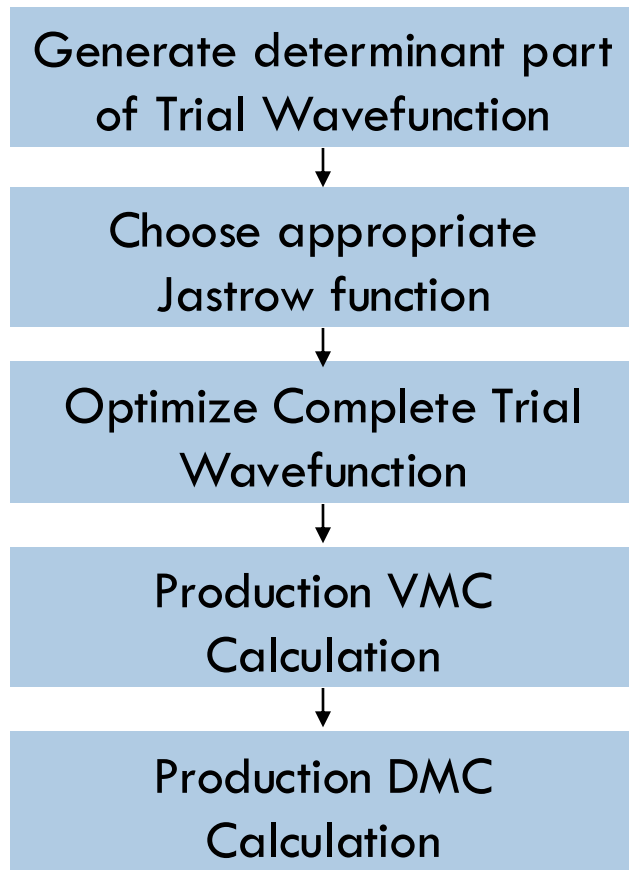
Variational solutions and Variational Monte Carlo

Wavefunction optimization

Diffusion Monte Carlo

Practicalities

Overall QMC workflow



Large basis set DFT, HF, CASSCF, CISD (etc.) calculation using standard DFT or QC code.
Standard recipe: 1 determinant only

Commonly just the Jastrow part, increasingly determinant and orbital coefficients as well

1st time: choose VMC & DMC timesteps

We can (and should) test all choices influencing the statistics

- If in doubt: run longer. Obtain better statistics.
- Use more sampled configurations in optimization.
- Allow for more equilibration time.
- Perform independent runs and verify the results agree to within error bars.

Once we are familiar with the statistical properties of one system, we can expect the same from other similar systems. E.g. Varying the lattice constant of a solid. The statistical properties result from the combination of algorithms, physics, and specific system studies.

Rough Guide to Monte Carlo Settings

Rough guidance for important for current science problems, methods and algorithms with typical wavefunctions:

VMC

Timestep ~ 0.5 a.u. (reasonable acceptance ratio, $\sim 40-60\%$)

Warmup/Equilibration ~ 100 steps
(be generous, VMC is “cheap”)

Resultant correlation period $\sim 1-10$ steps

Optimization samples $> 10^4$

Blocks > 100 (ease of analysis)

DMC

Timestep 0.01 a.u. (accuracy, stability)

Warmup/Equilibration $200+$ steps

Total walkers $\gg 10^3$, perhaps 10^4 .
Factor parallel and GPU efficiency.

Resultant correlation period $O(10^2)$ steps / 1 a.u.

Wavefunction Quality

Rough guide given current science problems, methods and algorithms. Test these choices when you first run a particular class of molecule or material.

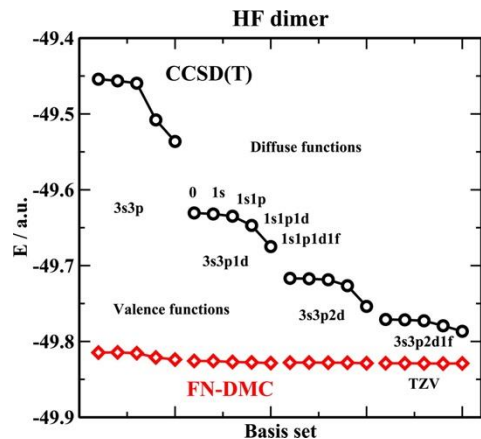
Single determinant starting point

Basis sets:

- Triple zeta Gaussians or better
- $\gg 100\text{Ry}$ plane waves, particularly with ccECPs

Jastrow function:

- 1,2,3 body (1,2 body do most of the work)
- 30-100 total variational parameters assuming DMC is eventual goal



HF dimer convergence

M. Dubecky et al.

Chem Rev. **116** 5188 (2016)

Rough Guide to Accessible System Sizes

Extremely subjective – if a large error bar is useful, ~any system size could be run.
If very high statistical accuracies are needed, larger resources are needed.
Calculations are formally N^3 scaling, statistics $\sim N^{2-4}$ depending on properties.

Electrons	Scale of Calculation
1-150	Powerful workstation/Single CPU node
150-500	Small Departmental Cluster
500+	Supercomputer

Assuming few 0.1 eV error bars, calculations on first 30 elements H-Zn, pseudopotentials, calculations of energy only.

Topics we did not cover

Statistics* (e.g. correlation, intensive vs extensive properties)

Pseudopotentials*

Periodic systems and finite size effects*

Advanced wavefunction forms – multideterminant, backflow, geminal, NN wavefunctions

Excited states

Observables – charge densities, density matrices, band inversion,... (we focused on energies here)

Workarounds for mixed-estimator problems in DMC

Other flavors of QMC (LRDMC, AFQMC, FCIQMC, neural network QMC)

*Covered in later sessions. We have materials on many of the other topics from recent workshops and previous tutorials.

Summary

Variational and diffusion quantum Monte Carlo are complementary statistical approaches for solving the Schrodinger equation.

VMC is simplest and places all the emphasis on the choice of trial wavefunction.

DMC is more powerful & more accurate, but more expensive, and has additional limitations.

Next session: Pseudopotentials, Workflows and statistical analysis

