

# QMC Workshop 2021

## Introduction to Quantum Monte Carlo

Week 2 / 12 October 2021

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[https://github.com/QMCPACK/qmc\\_workshop\\_2021](https://github.com/QMCPACK/qmc_workshop_2021)

Funding: U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, as part of the Computational Materials Sciences Program and Center for Predictive Simulation of Functional Materials.

# Outline

The electronic structure problem

Variational solutions and Variational Monte Carlo

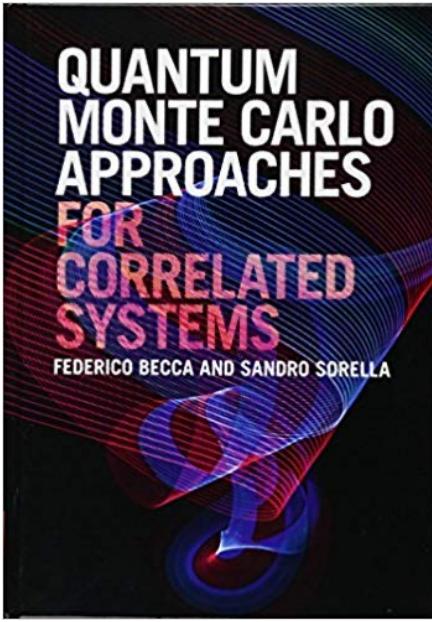
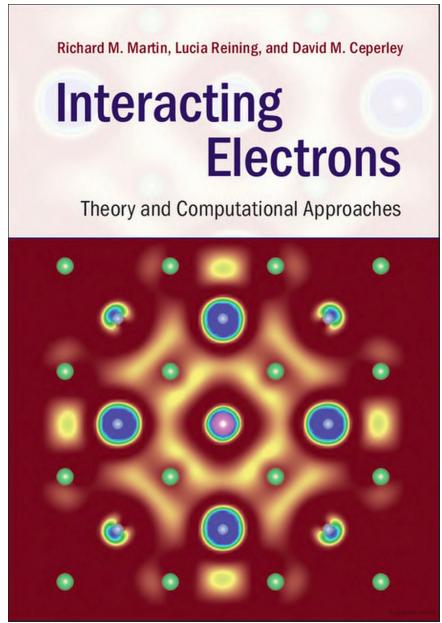
Wavefunction optimization

Diffusion Monte Carlo

Practical Matters

**Next week:** Workflows and statistical analysis presented by Jaron Krogel/ORNL

# Where to find more information



**JPC Publishing**  
J. Phys.: Condens. Matter 30 (2018) 195901 (29pp)  
<https://doi.org/10.1088/1361-648X/aad3d>

**QMCPACK: an open source *ab initio* quantum Monte Carlo package for the electronic structure of atoms, molecules and solids**

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Classic Review: W. Foulkes et al, Rev. Mod. Phys. **73** 33 (2001) [missing newer methods]  
M. Dubecky et al. Chem Rev. **116** 5188 (2016) [vdw molecules]  
QMCPACK citation: J. Kim et al, JPCM **30** 195901 (2018) [newer references, methods]  
update: P. R. C. Kent et al. JCP **152** 174105 (2020) [& other papers in the special issue]

# The Electronic Structure Problem

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

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

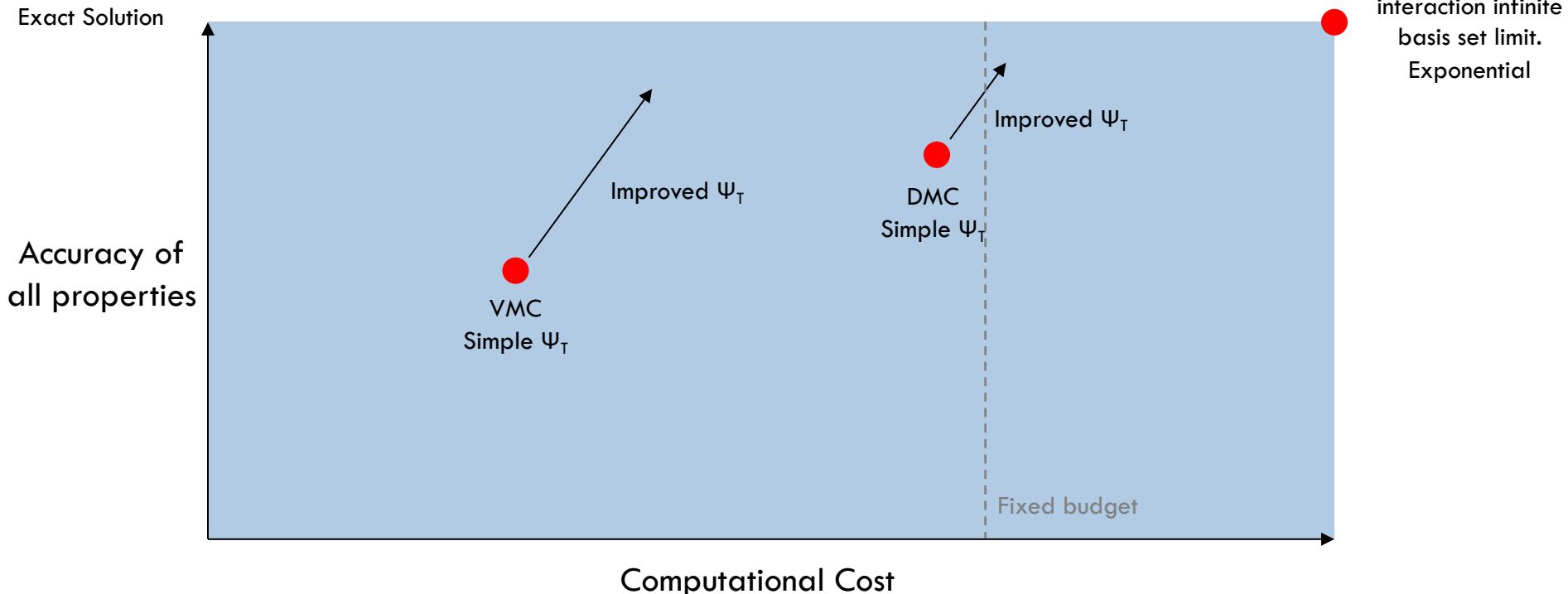
$$\hat{H} = -\frac{1}{2} \sum_i^{N_e} \nabla_i^2 - \sum_i^{N_e} \sum_{\alpha}^{N_{\alpha}} \frac{Z_{\alpha}}{|\mathbf{r}_i - \mathbf{d}_{\alpha}|} + \sum_i^{N_e} \sum_{j < i}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

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

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 hard” – we can’t expect to find a polynomial scaling or non-combinatorial scaling solution that is also exact.

# Convergence of 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

was formally exact but impractically exponentially scaling **QMC** Workshop 2021

# Outline

The electronic structure problem

Variational solutions and Variational Monte Carlo

Wavefunction optimization

Diffusion Monte Carlo

Practical Matters

# 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 good  $\Psi_T$  and methods to 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:

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

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 $|\Psi|^2$ 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:

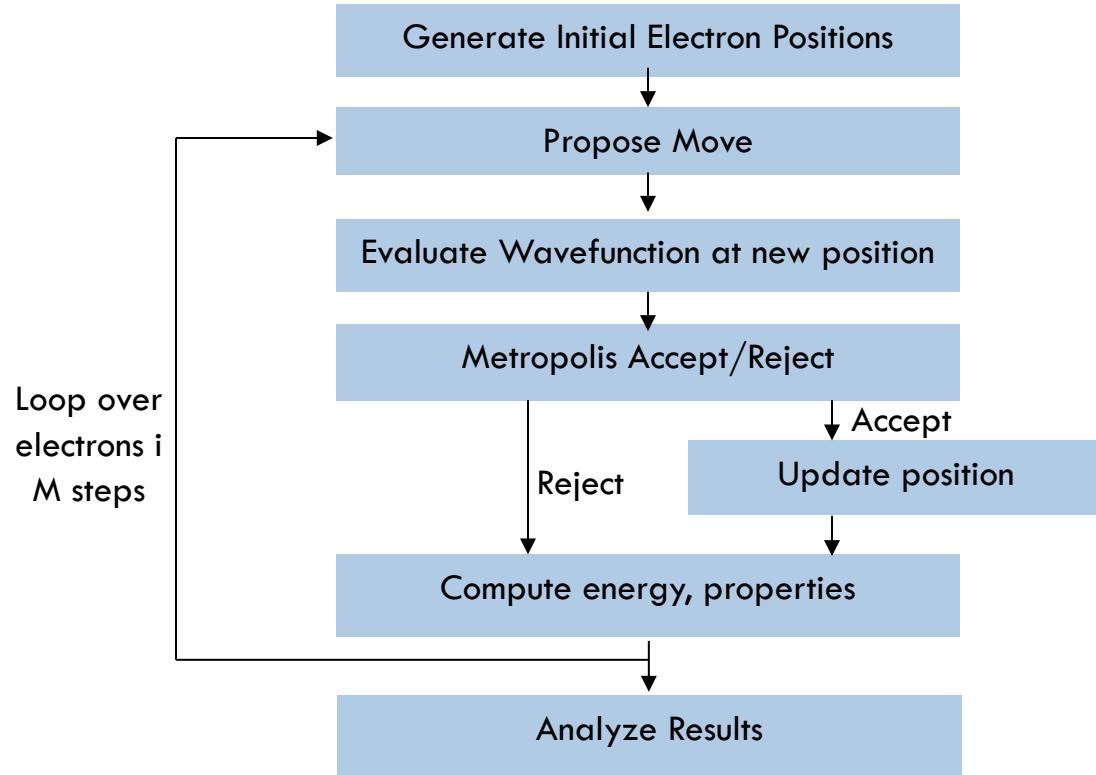
For every electron i:

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 Gaussian-distributed proposed moves, width proportional to an input “timestep”.

# Variational Monte Carlo Algorithm



## Key measured properties

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

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

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

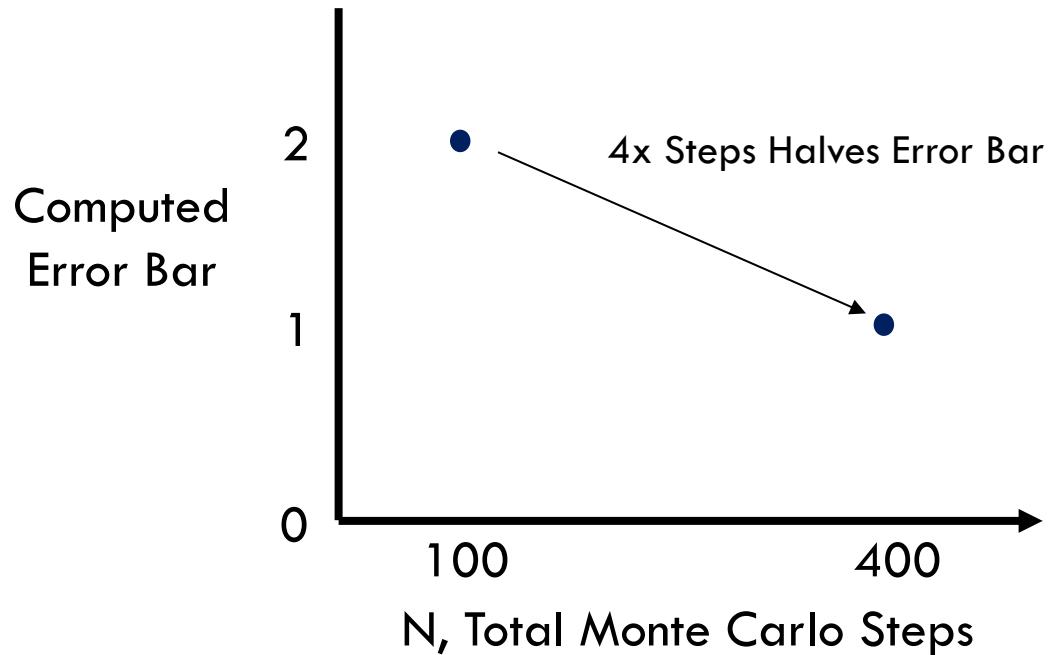
Variance  $\sigma^2$ : measure of width of energy distribution.

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

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  $\{p\}$ . Jastrow factor improves accuracy over HF determinant or CI expansion alone.

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


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  $c$ . (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.

$$\begin{aligned} J(\{\mathbf{r}_i\}, \{\mathbf{r}_I\}) = & \sum_{i=1}^{N-1} \sum_{j=i+1}^N u(r_{ij}) + \sum_{I=1}^{N_{\text{ions}}} \sum_{i=1}^N \chi_I(r_{il}) \\ & + \sum_{I=1}^{N_{\text{ions}}} \sum_{i=1}^{N-1} \sum_{j=i+1}^N f_I(r_{il}, r_{jl}, r_{ij}) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N p(\mathbf{r}_{ij}) \\ & + \sum_{i=1}^N q(\mathbf{r}_i), \end{aligned}$$

Drummond et al. PRB **70** 235119 (2004)

# 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:

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

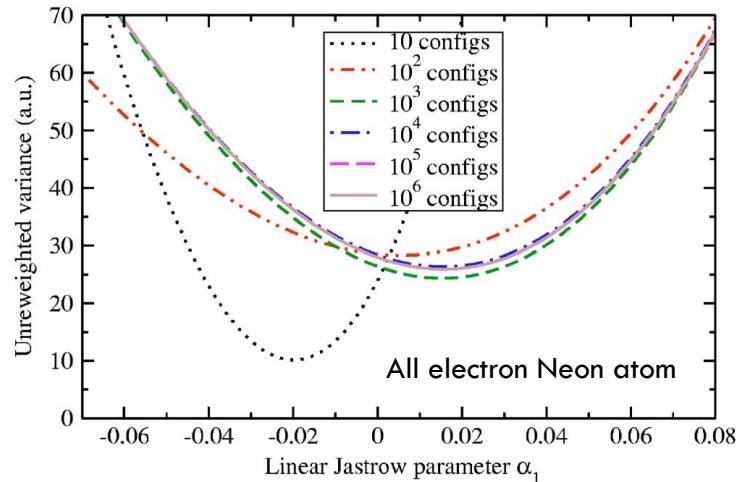
$$\frac{\sigma^2}{M} \approx \frac{1}{M(M-1)} \sum_{m=1}^M \left( E_L(\mathbf{R}_m) - \left( \frac{1}{M} \sum_{m=1}^M E_L(\mathbf{R}_m) \right) \right)^2$$

$$\sigma^2 \geq 0$$

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  $\sigma^2$  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.

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

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

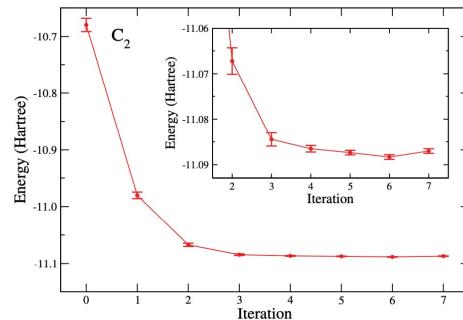
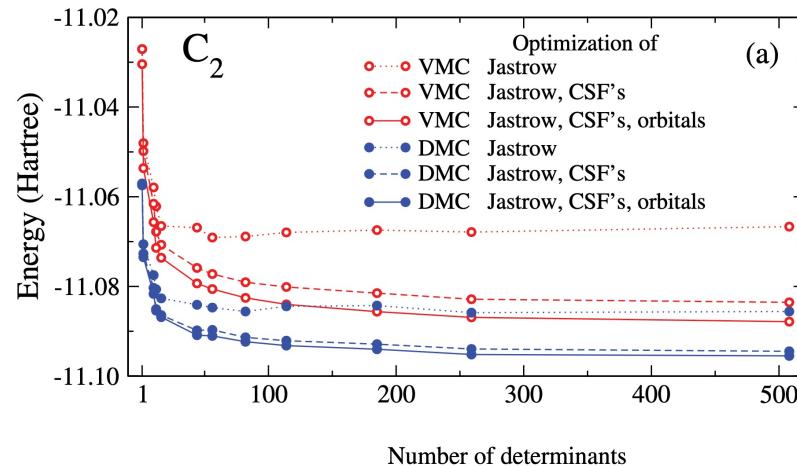


FIG. 1 (color online). Convergence of the VMC total energy of the  $C_2$  molecule when simultaneously optimizing 24 Jastrow, 73 CSF and 174 orbital parameters for a truncated CAS(8,14) wave function. The number of MC configurations range from 10 000 for the first iteration to 400 000 for the last iterations.



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

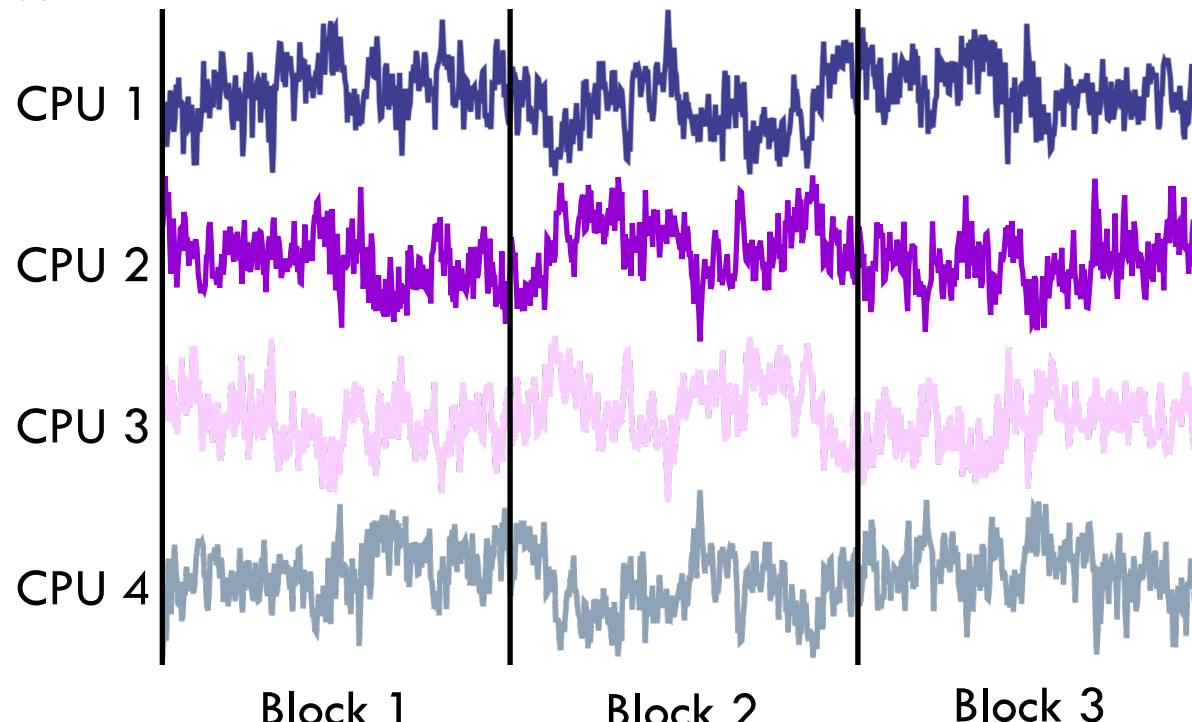
C. J. Umrigar et al. PRL 98 110201 (2007)

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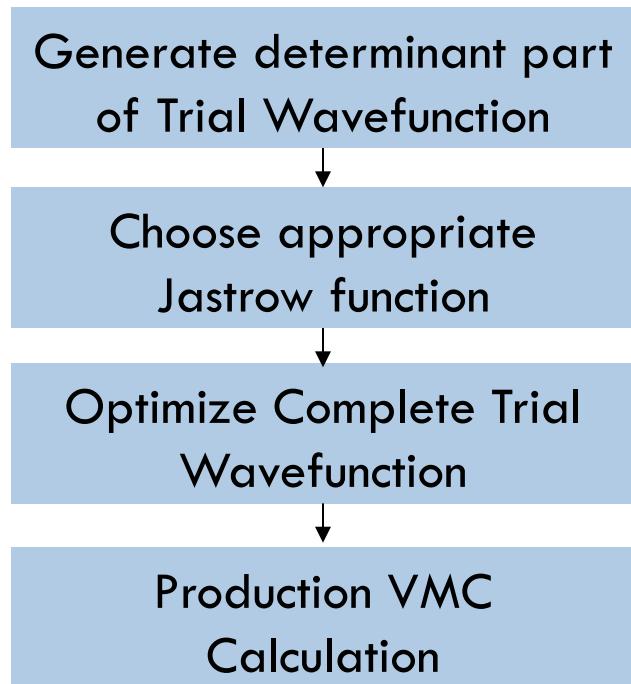
# Mapping VMC to computers

Simply put one independent “walker”/Markov chain on each core (or thread)

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



# VMC workflow



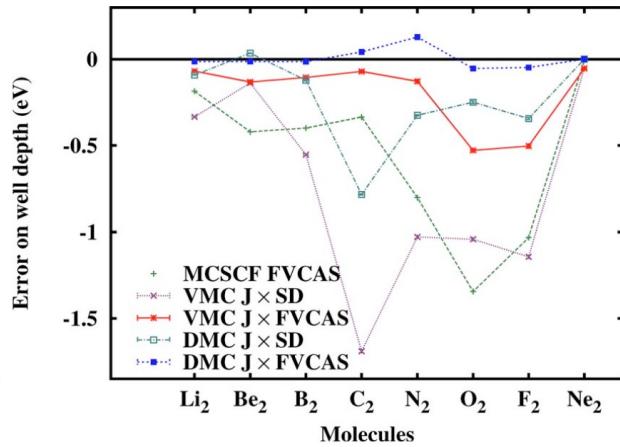
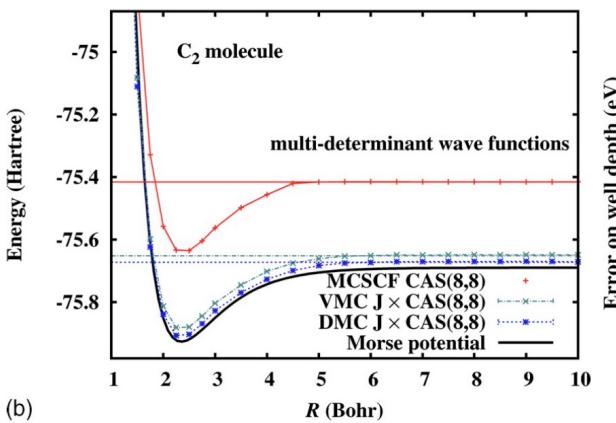
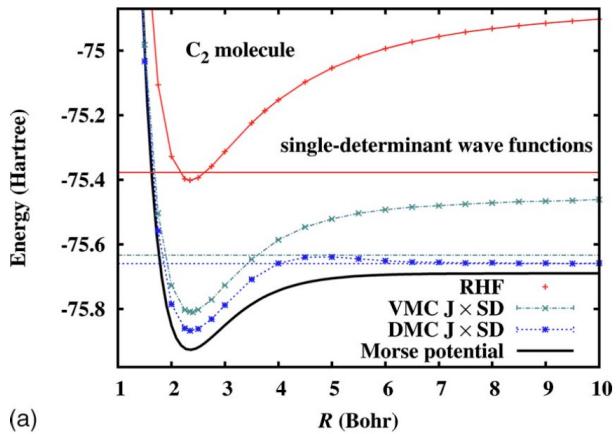
Large basis set DFT, HF, CASSCF, CI calculation using standard DFT or QC code

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

1<sup>st</sup> time through: choose timestep, try different Jastrow functions

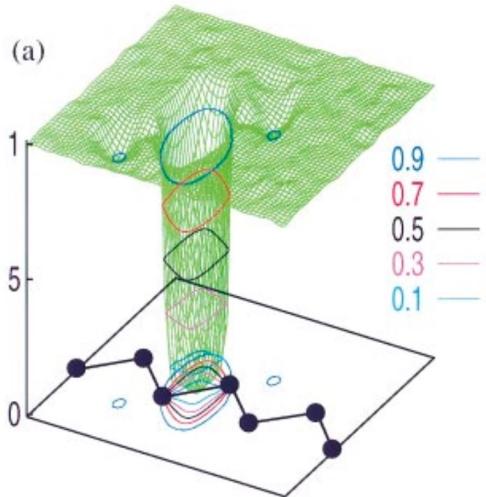
# Example VMC Calculations

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



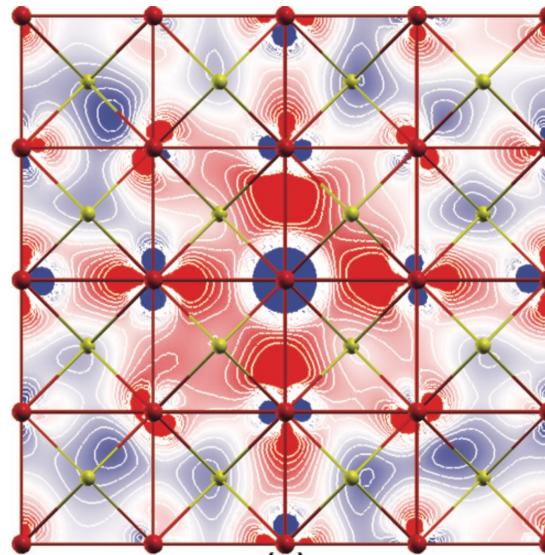
# Example VMC Calculations (advanced!)

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



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

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



Pairing function in FeSe Superconductors  
Casula & Sorella PRB **88** 155125 (2013)

# Key features of VMC

Advantages	Disadvantages
<p>Explicit form of trial wavefunction</p> <ul style="list-style-type: none"><li>• Can use any trial wavefunction we can imagine, motivated by physics/chemistry, not ease of integration.</li><li>• Can directly compute any observable.</li><li>• Simple Monte Carlo – no timestep error or other discretization introduced.</li><li>• Nominally cubic scaling with system size.</li></ul>	<p>Explicit form of trial wavefunction</p> <ul style="list-style-type: none"><li>• Limited to forms of trial wavefunction we can imagine - high accuracy difficult for solids, correlated physics, may not have consistent errors.</li><li>• Potentially many parameters to optimize reliably. Not yet automated/“push button”.</li></ul> <p>All QMC methods: Need to perform finite size scaling even for primitive cells in periodic calculations.</p>

# **Break**

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Wavefunction optimization

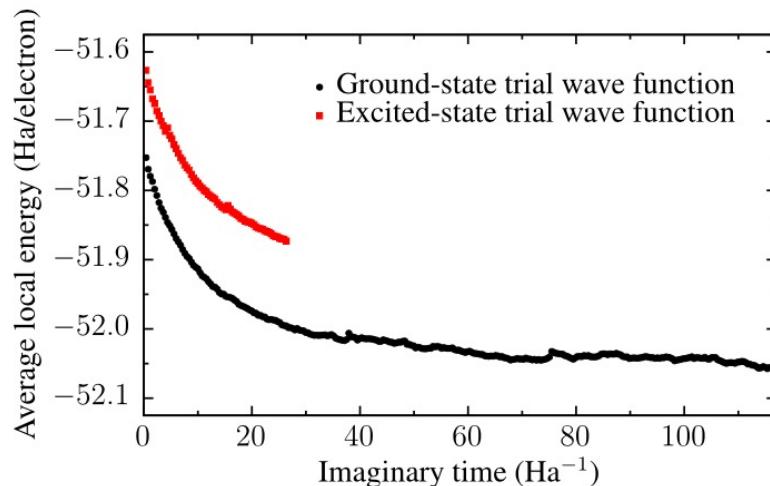
Diffusion Monte Carlo

Practical Matters

# 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  $\tau$  all 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

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

Walkers drift,  
diffuse &  
renormalize

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

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

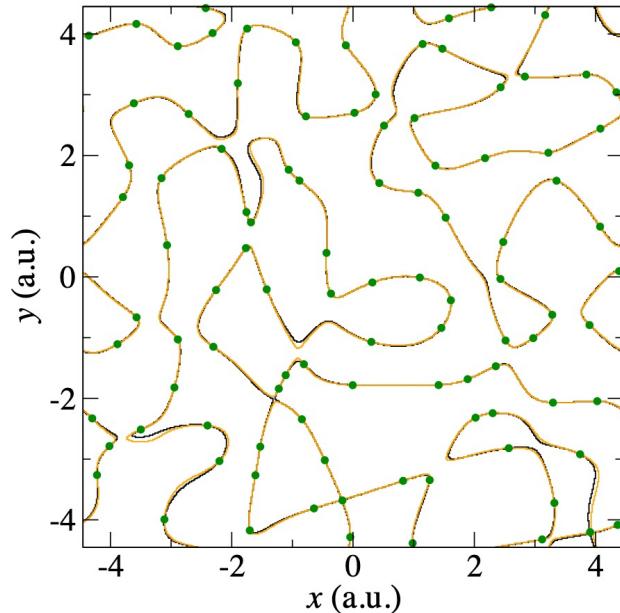
# Fixed Node Approximation

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

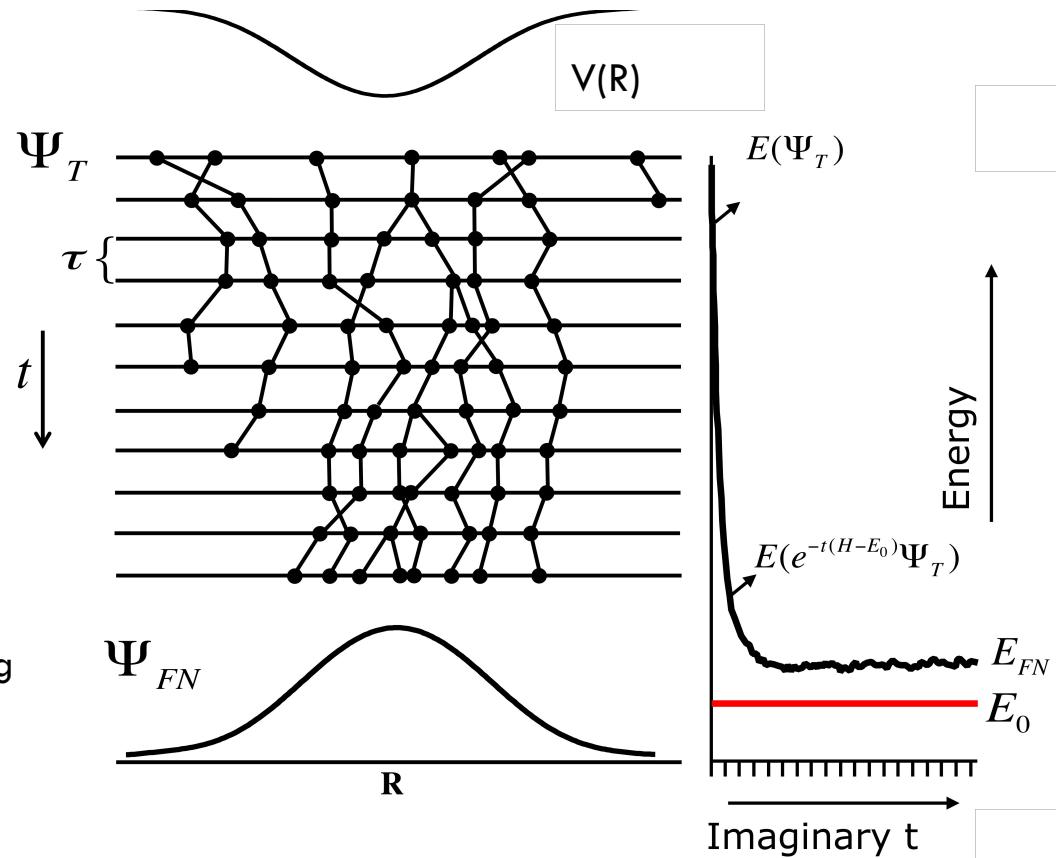
DMC algorithm maps onto a time varying population of walkers where walkers in energetically favorable locations multiply and walkers in unfavorable locations are removed.  
(Can use weights equivalently).

To run DMC we need:

- Input trial wavefunction
- Time step (smaller = more accurate)
- Target population

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

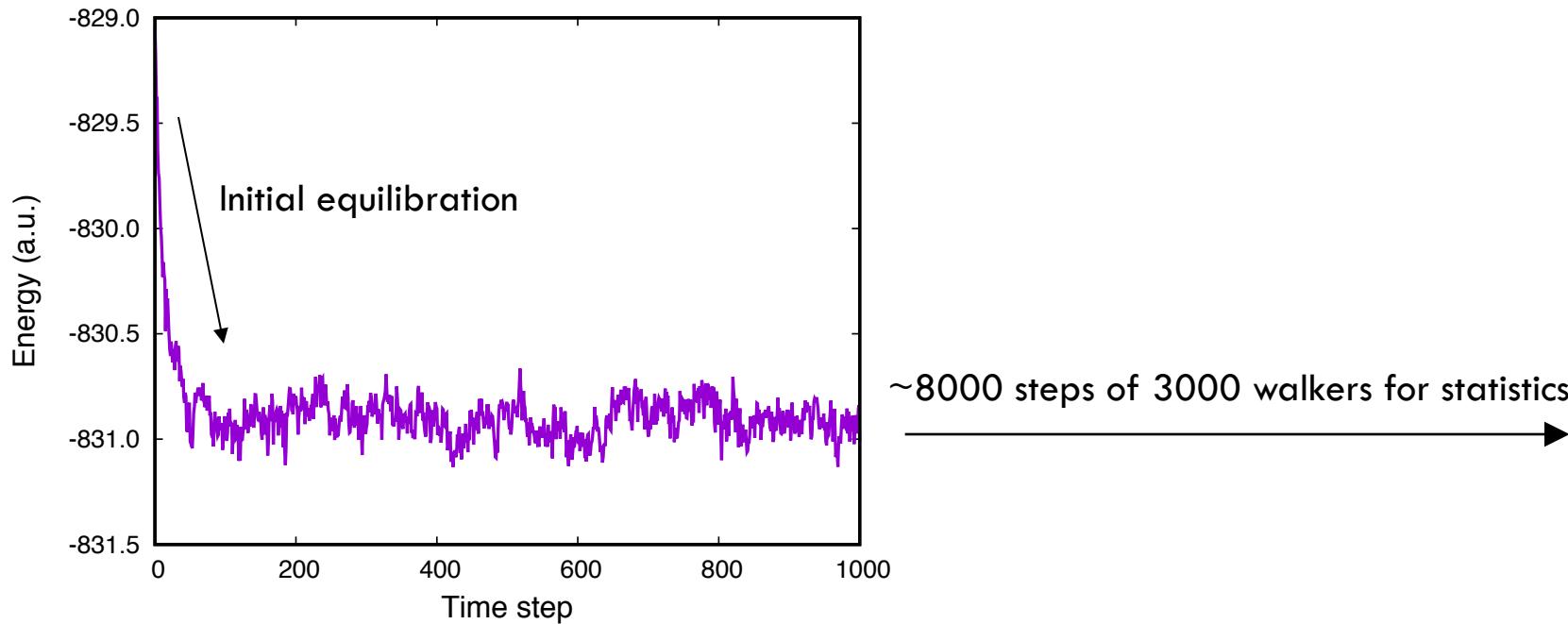
(Not shown) Target/trial energy is updated smoothly to keep population near target value.



# Real-world DMC: Bulk VO<sub>2</sub>

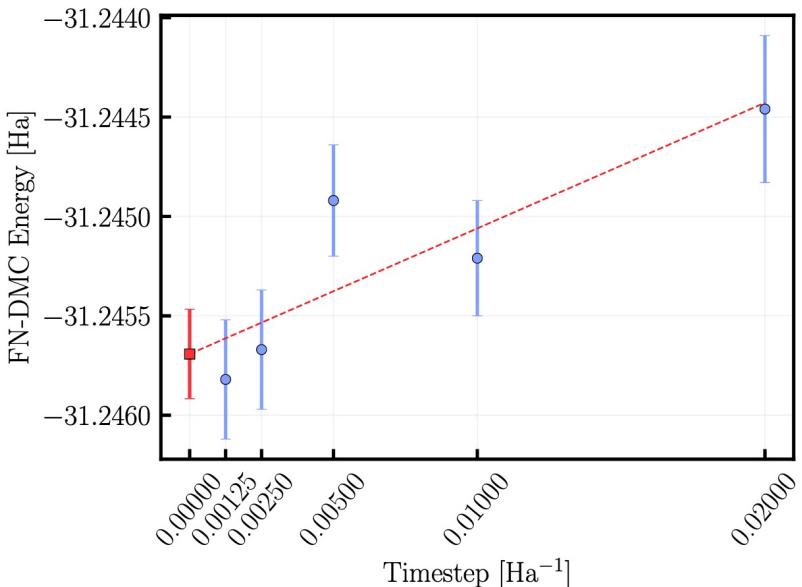
Given an input trial wavefunction (and its nodal surface), time-step, and population size we can run DMC

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

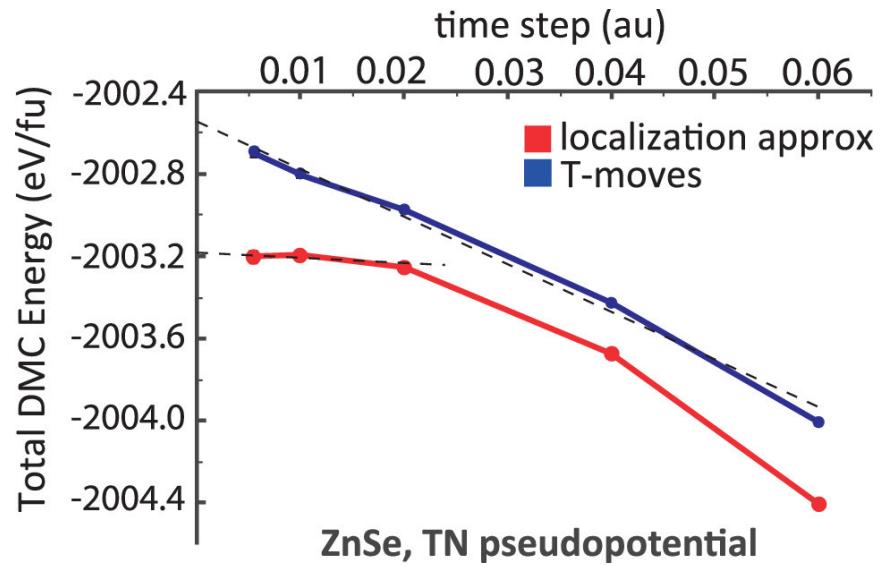


# Time Step Errors

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



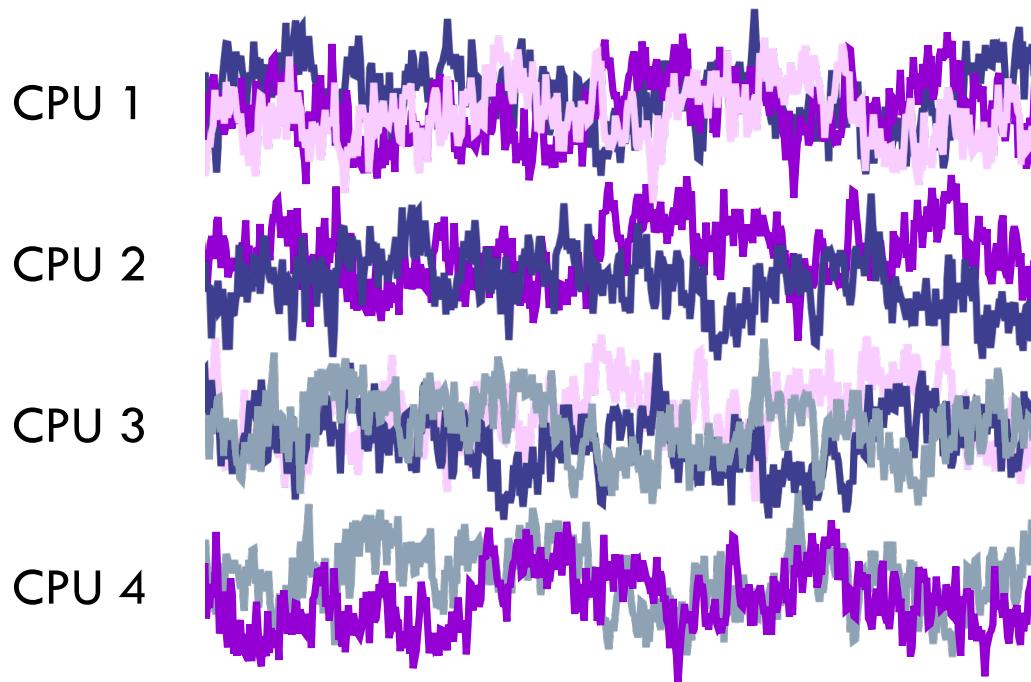
“Bulk silicon benchmarks and systematic control of biases”. Annaberdiyev et al. PRB **103** 205206 (2021)



“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

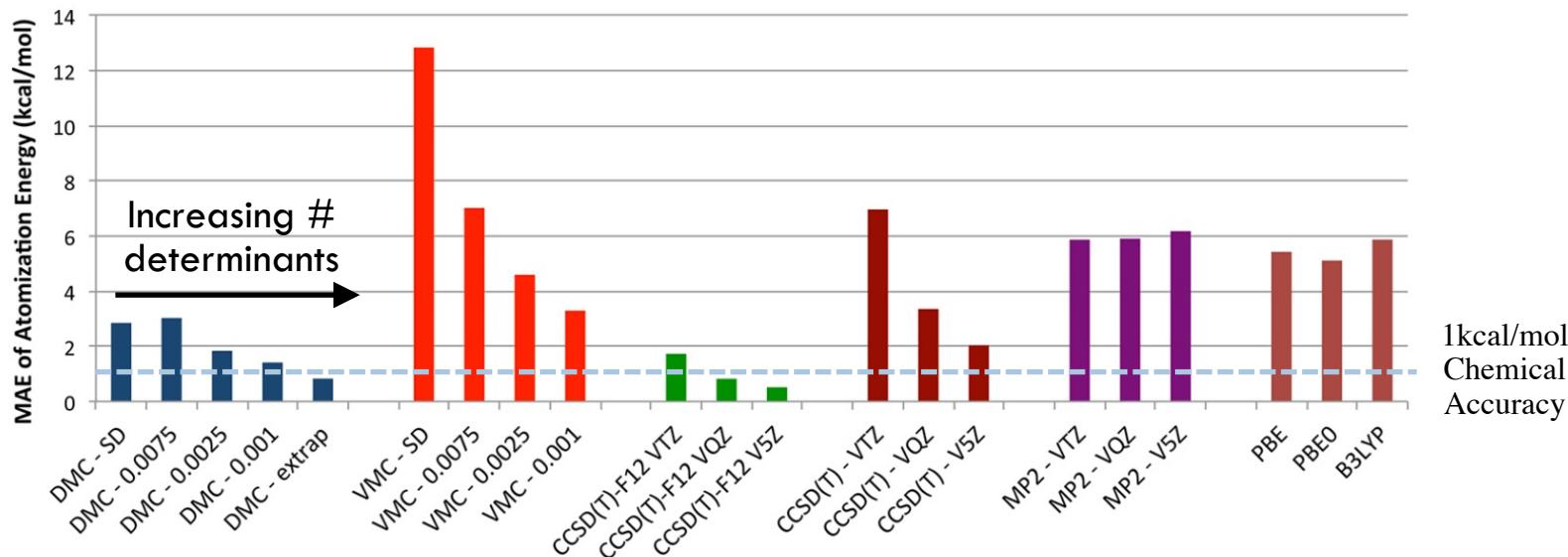
Put many “walkers”/Markov chains on each core. Overall average energy needed for population control/normalization is updated ~every step. Write out average energies each step. Some implementations have variable number of walkers per core, potentially resulting in load imbalance.



# Example DMC & VMC for Molecular Calculations

Chemical accuracy <1kcal/mol achieved via the “linear method” for wf optimization.

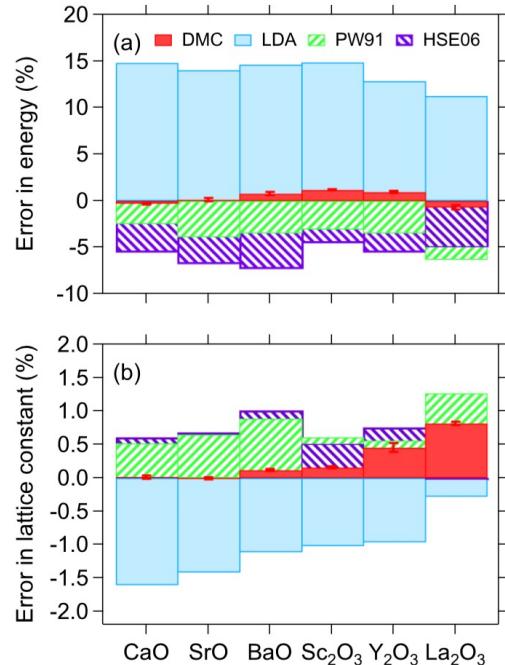
Trial wavefunctions use large multideterminant expansions. DMC better than VMC.



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

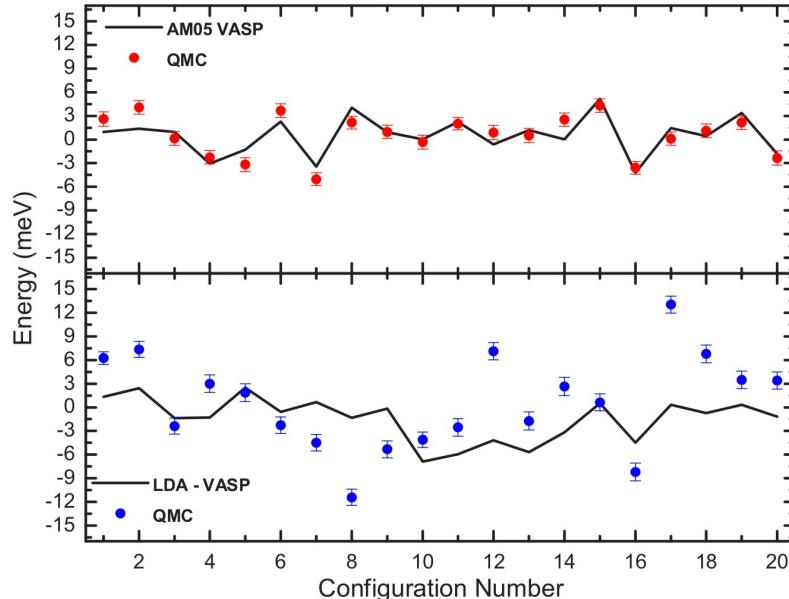
# Example DMC Calculations

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



Kr liquid at high pressure: AM05 functional found to have best agreement with QMC.

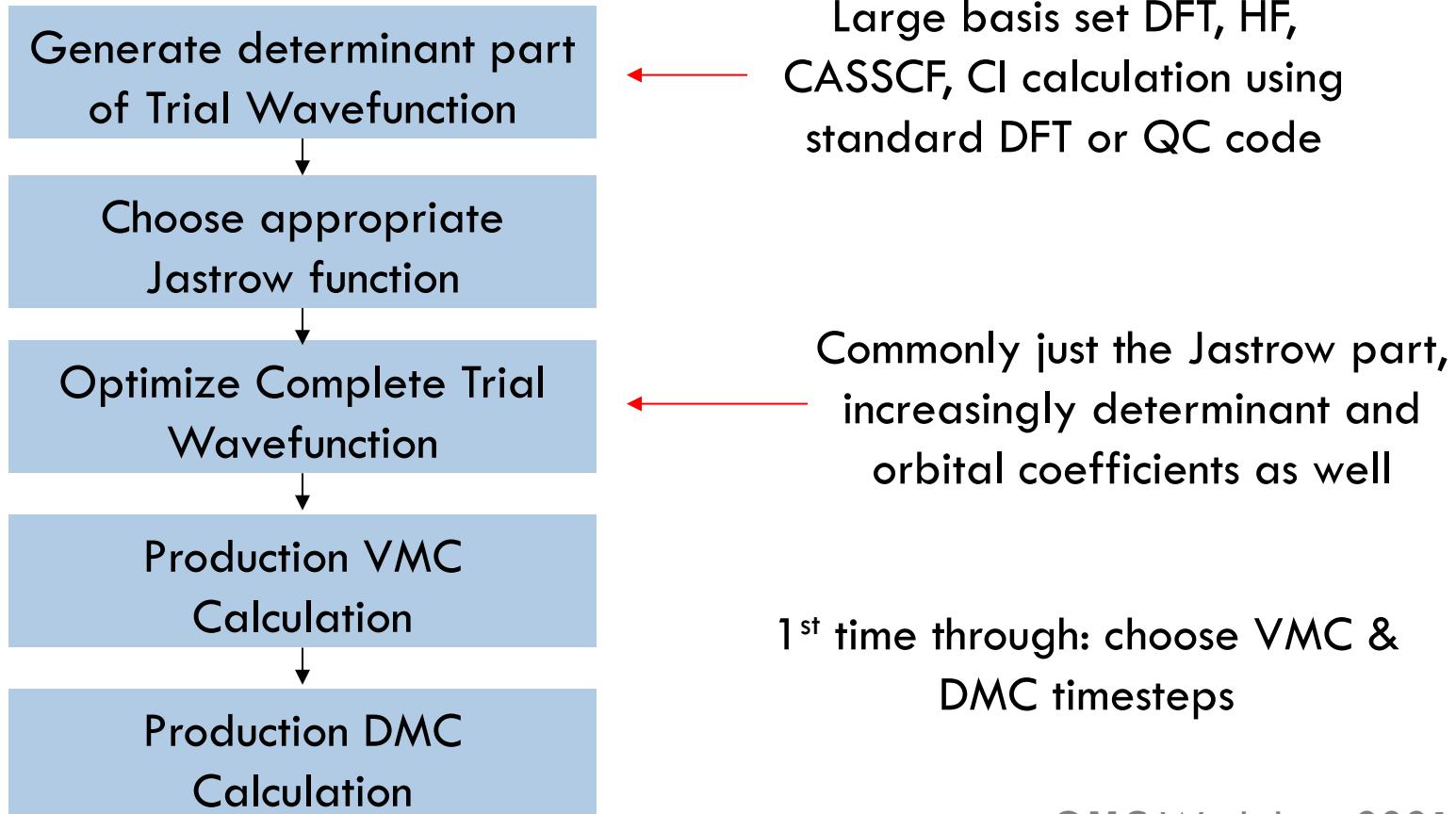
Use AM05 for large scale dynamics.  
Mattsson et al. PRB **90** 184105 (2014)



# Key features of DMC

Advantages	Disadvantages	Errors, Approximations
<p>Gives very accurate and robust results, even with simple nodal surfaces/trial wavefunctions.</p> <p>Easily takes advantages of supercomputers.</p> <p>Improveable with better quality trial wavefunctions.</p>	<p>Unlike VMC, no explicit wavefunction obtained. Mixed estimator problem for non-commuting observables.</p> <p>Significantly more expensive than VMC.</p> <p>Small timestep needed for high Z elements.</p> <p>Finite size scaling &amp; cost in solid-state (Supercells).</p>	<p>“Fixed node” variational error in energy is key approximation.</p> <p>Approximations are potentially all controllable (also applies to VMC).</p> <p>Non-local pseudopotentials need special treatment.</p>

# Overall QMC workflow



# We can test all choices influencing the statistics

- Run longer. Obtain better statistics.
- Use more samples in optimization.
- Allow for more equilibration time.
- Perform independent runs and verify the results agree (to within error bars).

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

# Rough Guide to Monte Carlo Settings

Rough guidance for typically used orders of magnitude for 2021 era science problems, methods and algorithms:

## VMC

Timestep  $\sim 0.5$  a.u. (reasonable acceptance ratio,  $\sim 40\text{-}60\%$ )  
Warmup/Equilibration  $\sim 100$  steps (be generous, VMC is “cheap”)  
Blocks  $> 100$  (ease of analysis)  
Optimization samples  $> 10^4$   
Resultant correlation period  $\sim 1\text{-}10$

## DMC

Timestep 0.01 a.u. (accuracy, stability)  
Warmup/Equilibration 200 steps  
Total walkers  $> 10^3$   
Resultant correlation period  $\sim 10^2$

# Wavefunction Quality

Rough guide to given 2021 era science problems, methods and algorithms

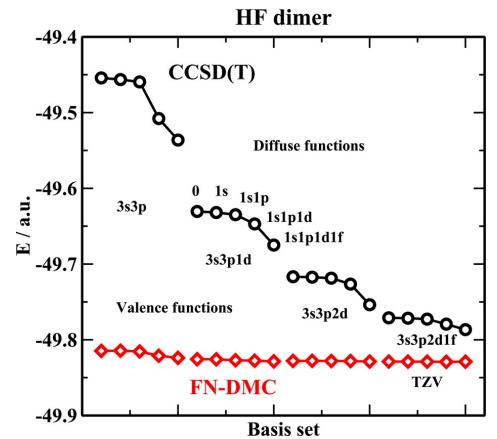
Basis sets:

- Triple zeta Gaussians or better
- $>>100\text{Ry}$  plane waves

Single determinant starting point

Jastrow function:

- 1,2,3 body (1,2 body do most of the work)
- 20-100 total variational parameters assuming DMC is eventual goal



HF dimer convergence  
M. Dubecký et al.  
Chem Rev. **116** 5188 (2016)

# 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
1-100	Powerful workstation
100-400	Departmental Cluster
400+	Supercomputer

Assuming few 0.1 eV error bars, calculations on first 30 elements H-Zn

# Topics we did not cover

Statistics in depth\* (e.g. intensive vs extensive properties)

Pseudopotentials\*

Finite size effects\*

Advanced wavefunction forms – multideterminant\*, backflow, geminal wavefunctions

Why forces are difficult to compute accurately & cheaply

Workarounds for mixed-estimator problems in DMC

Excited states

Other flavors of QMC

...

\*Covered in later weeks. Many of the other topics were covered during our 2019 workshop and could be revisited in 2022.

# 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 week:** Workflows and statistical analysis presented by Jaron Krogel/ORNL

