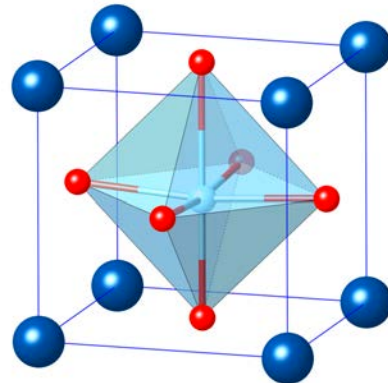
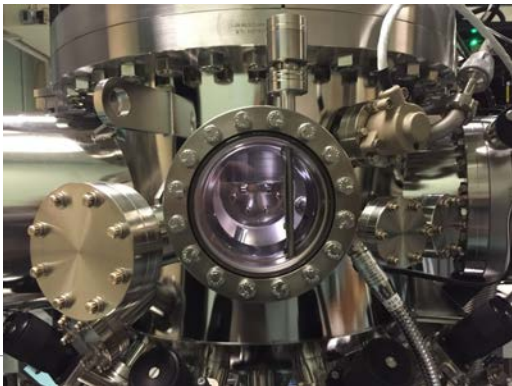


Quantum Monte Carlo for Real Materials

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Outline

- Motivation
- Introduction to QMC methods
- Examples of today's capabilities
- Future directions. Speculative!

Questions are welcome

Acknowledgements

All the members of the Center for Predictive Simulation of Functional Materials.
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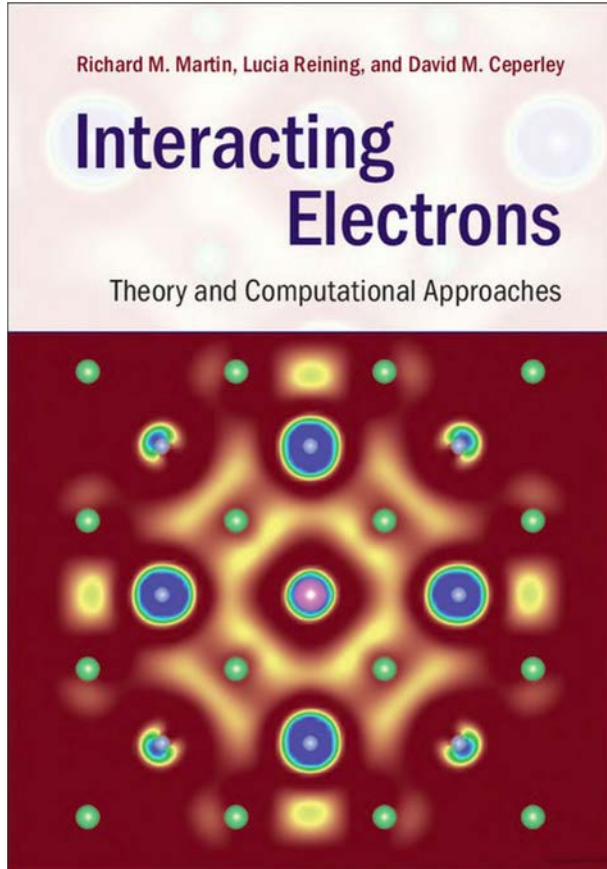
NCSU

L. Mitas

M. C. Bennett

C. Melton

Further reading



Quantum Monte Carlo simulations of solids

W. M. C. Foulkes

CMTH Group, Department of Physics, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BZ, United Kingdom

L. Mitás

National Center for Supercomputing Applications, University of Illinois at Urbana-Champaign, Urbana-Champaign, Illinois 61801 and Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202

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 wave-function-based approaches provide a very direct treatment of quantum many-body effects and serve as benchmarks against which other techniques may be compared. They complement the less demanding density-functional approach by providing more accurate results and a deeper understanding of the physics of electronic correlation in real materials. The algorithms are intrinsically parallel, and currently available high-performance computers allow applications to systems containing a thousand or more electrons. With these tools one can study complicated problems such as the properties of surfaces and defects, while including electron correlation effects with high precision. The authors provide a pedagogical overview of the techniques and describe a selection of applications to ground and excited states of solids and clusters.

IOP Publishing

Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **30** (2018) 195901 (29pp)

<https://doi.org/10.1088/1361-648X/aa98c3>

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

Jeongnim Kim¹, Andrew T Baczewski², Todd D Beaudet³, Anouar Benali^{4,5}, M Chandler Bennett⁶, Mark A Berrill⁷, Nick S Blunt⁸, Edgar Josué Landinez Borda⁹, Michele Casula¹⁰, David M Ceperley¹¹, Simone Chiesa¹¹, Bryan K Clark¹¹, Raymond C Clay III¹², Kris T Delaney¹², Mark Dewing¹³, Kenneth P Esler¹³, Hongxia Hao¹⁴, Oile Heinonen^{15,16}, Paul R C Kent^{17,18}, Jaron T Krogel¹⁹, Ilkka Kylänpää¹⁹, Ying Wai Li²⁰, M Graham Lopez¹, Ye Luo^{4,5}, Fionn D Malone⁹, Richard M Martin¹¹, Amrita Mathuriya¹, Jeremy McMinis⁹, Cody A Melton⁶, Lubos Mitás⁶, Miguel A Morales⁹, Eric Neuscamman^{21,22}, William D Parker²³, Sergio D Pineda Flores²¹,

Book: “Interacting Electrons”, Martin, Reining, Ceperley
Review: W. Foulkes et al, Rev. Mod. Phys. **73** 33 (2001) [real space only, older]
Code citation: J. Kim et al, JPCM **30** 195901 (2018) [has newer references, methods]

Dirac's Challenge



“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

Proceedings of the Royal Society (1929)

Our challenge

Solve the many-body Schrodinger equation with only readily controllable approximations

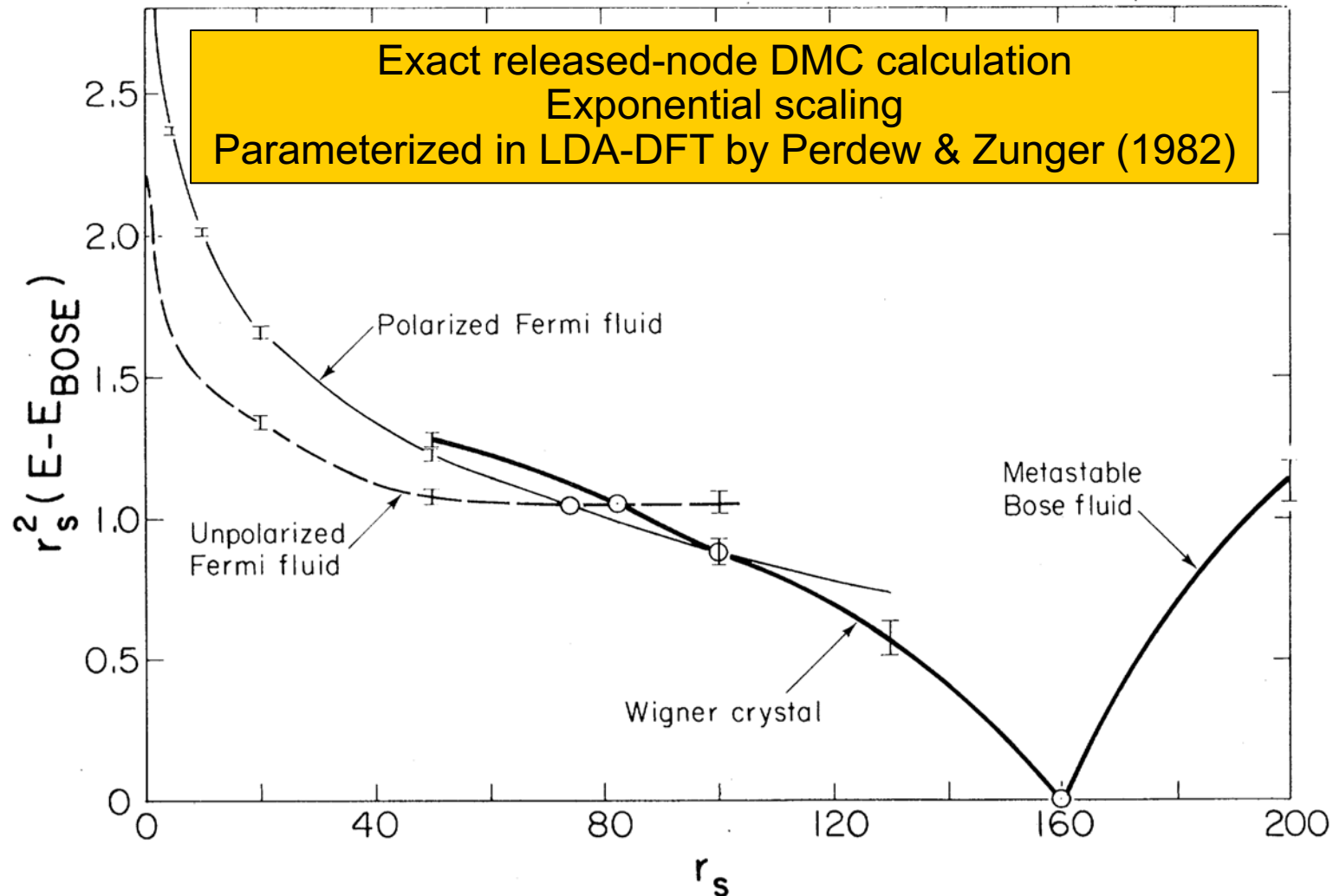
Our Goal

Develop an accurate and tractable convergent method for real materials and chemistry

Understand many-body physics, chemistry, materials

Provide useful benchmarks of other methods, particularly for periodic systems, and eventual upscaling

Exact QMC results for the Homogeneous Electron Gas

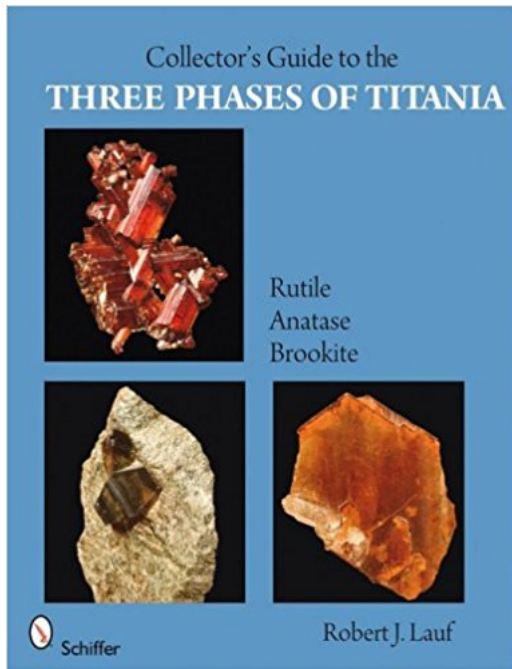


Ceperley & Alder PRL **45** 566 (1980)

See N. Tubman et al. JCP **135** 184109 (2011) for discussion of modern prospects

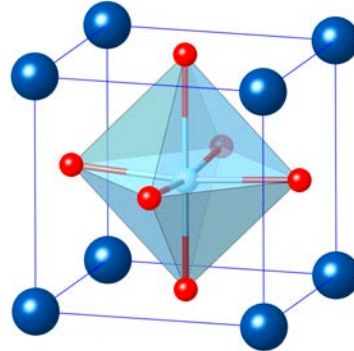
Experiment is not perfect...

Sometimes unclear



Multiple TiO_2 metastable phases, importance of growth conditions complicates ground state analysis. Common problem!

Sometimes unavailable



Predicted new materials

Difficult:
Defect energies
Novel pressures,
Novel temperature,
...

Sometimes unique and expensive



Juno@Jupiter

Wahl et al. GRL (2017)

“...interior models based on ab initio computer simulations of hydrogen-helium mixtures...”

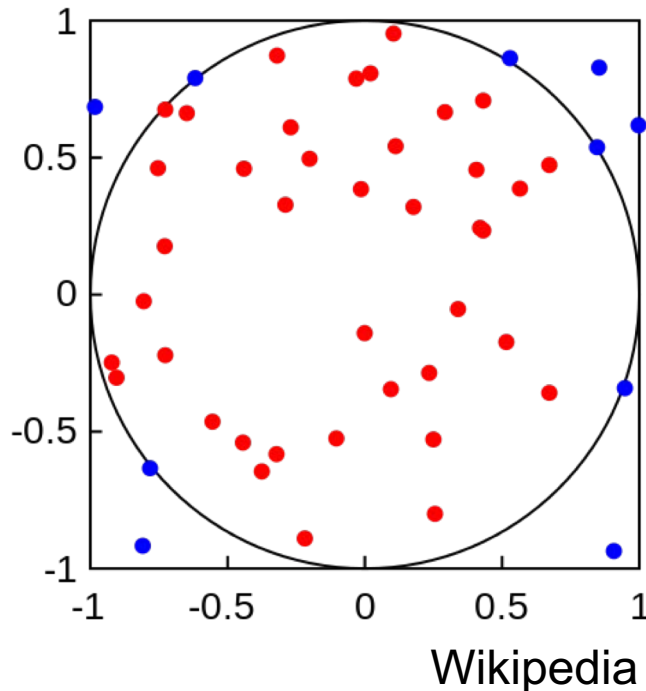
Outline

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- Introduction to QMC methods
- Examples of today's capabilities
- Future directions. Speculative!

Monte Carlo Methods

Tackle the numerical complexity of the Schrodinger equation via statistical methods, e.g. Monte Carlo integration. MC is more efficient than numerical integration in high dimensions.

Trade-off: all measurements have a *statistical error*.



Estimate pi via random sampling and ratio of points inside circle to square.

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

100x increase in cost to reduce error 10x !
High-quality importance sampling needed
Plan calculations carefully!

Flavors of Quantum Monte Carlo

- Real space QMC
 - Sample electron positions in real space
 - Variational, diffusion, reptation...
 - Longest established, most results
- Auxiliary Field QMC Motta & Zhang <http://arxiv.org/abs/1711.02242>
 - Works in a basis. Strong basis set effects.
 - Easier access to observables than DMC
 - Appears more accurate by default than DMC, but larger cost prefactor. Fewer results.
- Full Configuration Interaction QMC
 - Works in determinants
 - Near exact, expensive. Booth et al. Nature **493** 365 (2013)

Variational Monte Carlo

Use Monte Carlo integration to obtain a variational energy bound from a trial wavefunction. Optimize parameters in trial to reduce variational energy and improve trial wavefunction.

$$E_T = \frac{\int \Psi_T^* \hat{H} \Psi_T}{\int |\Psi_T|^2} \geq E_0$$

$$\Psi_T = \sum_i c_i D_i e^J$$

Use best available physics-motivated trial e.g. Sum of determinants. Great flexibility: only need to evaluate value & derivatives in real space

$$E_T = \frac{\int |\Psi_T|^2 \frac{\hat{H} \Psi_T}{\Psi_T}}{\int |\Psi_T|^2}$$

First part is a probability density: positive definite & normalized
We can do textbook Metropolis Monte Carlo
For 1000 electrons = 3000 dimensional integral
Avoid recomputing entire trial wavefunction to make efficient

Modern trial wavefunctions

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



Use the best affordable density functional or quantum chemistry wavefunction. Reoptimize some or all coefficients.



Parameterized real-space Jastrow correlation factor. Build in physics, e.g. e-e and e-n cusps. *Greatly* improves trial wavefunction. Does not change nodes

Solids

Today mostly single determinant from DFT + Jastrow due to numerical & statistical limitations

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

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

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

$$+ \sum_{i=1}^N q(\mathbf{r}_i),$$

Other options: Backflow, Geminals...

Key features of VMC

Advantages

Explicit form of trial wavefunction

- Can use any trial wavefunction we can imagine
- Easy to compute any observable
- Simple Monte Carlo – no timestep error or other discretization introduced

Disadvantages

Explicit form of trial wavefunction

- Limited to forms of trial wavefunction we can imagine - high accuracy difficult for solids, correlated physics.
- Potentially many parameters to optimize reliably. Not yet automated.

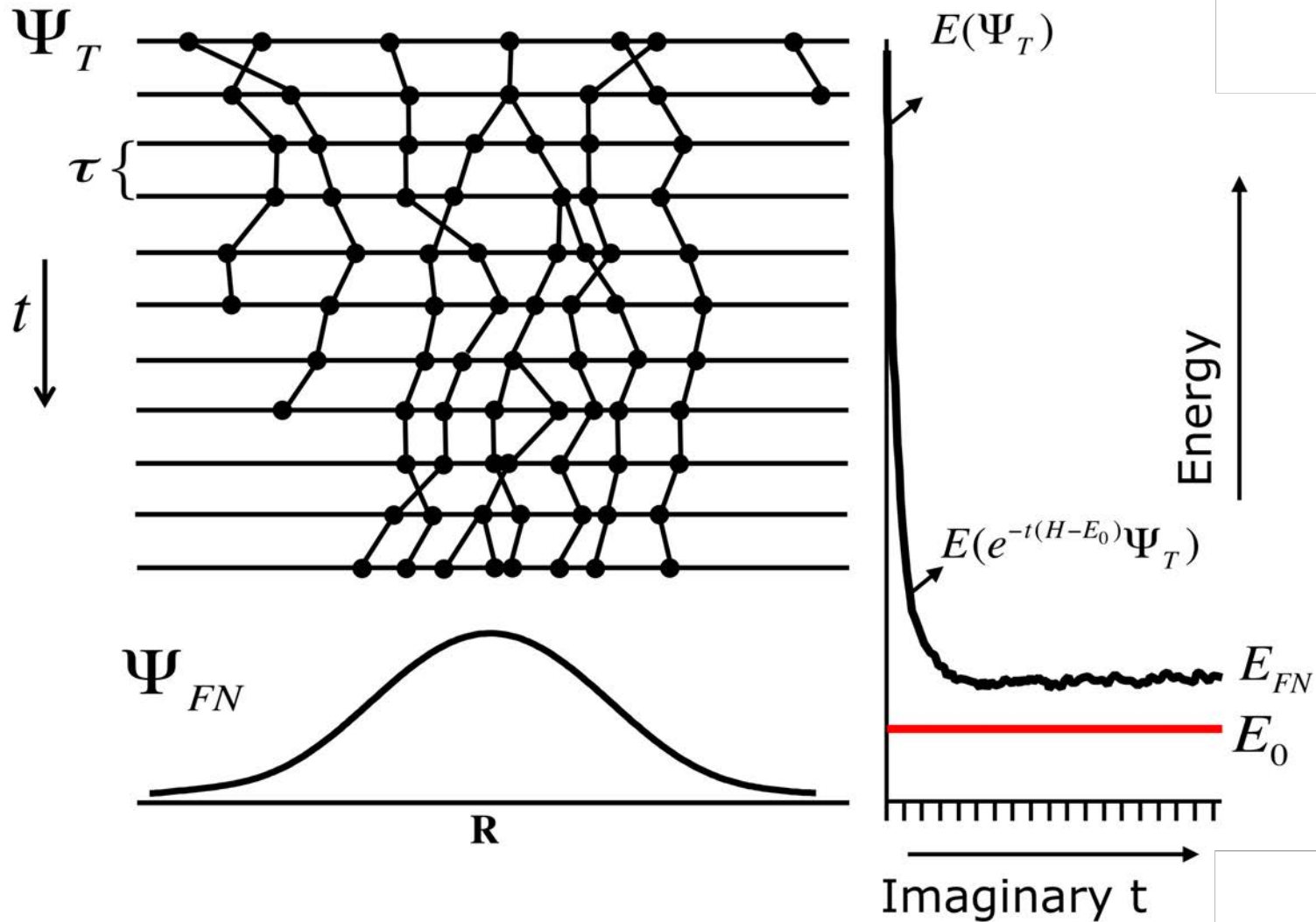
Diffusion Quantum Monte Carlo

- A many-body wavefunction **projection** method; minimizes trial wavefunction dependence by projecting out ground state
- Write the time dependent Schrodinger equation in **imaginary time**

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

- Maps to a branching importance sampled Monte Carlo evolving in time
- Enforce a fermionic solution via the “**fixed-node approximation**”. Fix nodes of projected wavefunction to be the same as a trial wavefunction. Variational error in energy. **Most significant approximation in DMC.**
- Leads to a robust method with good properties: variational, accurate - yields high-fraction of correlation energy, formally N^2 - N^4 scaling, readily parallelized...

Cartoon Example

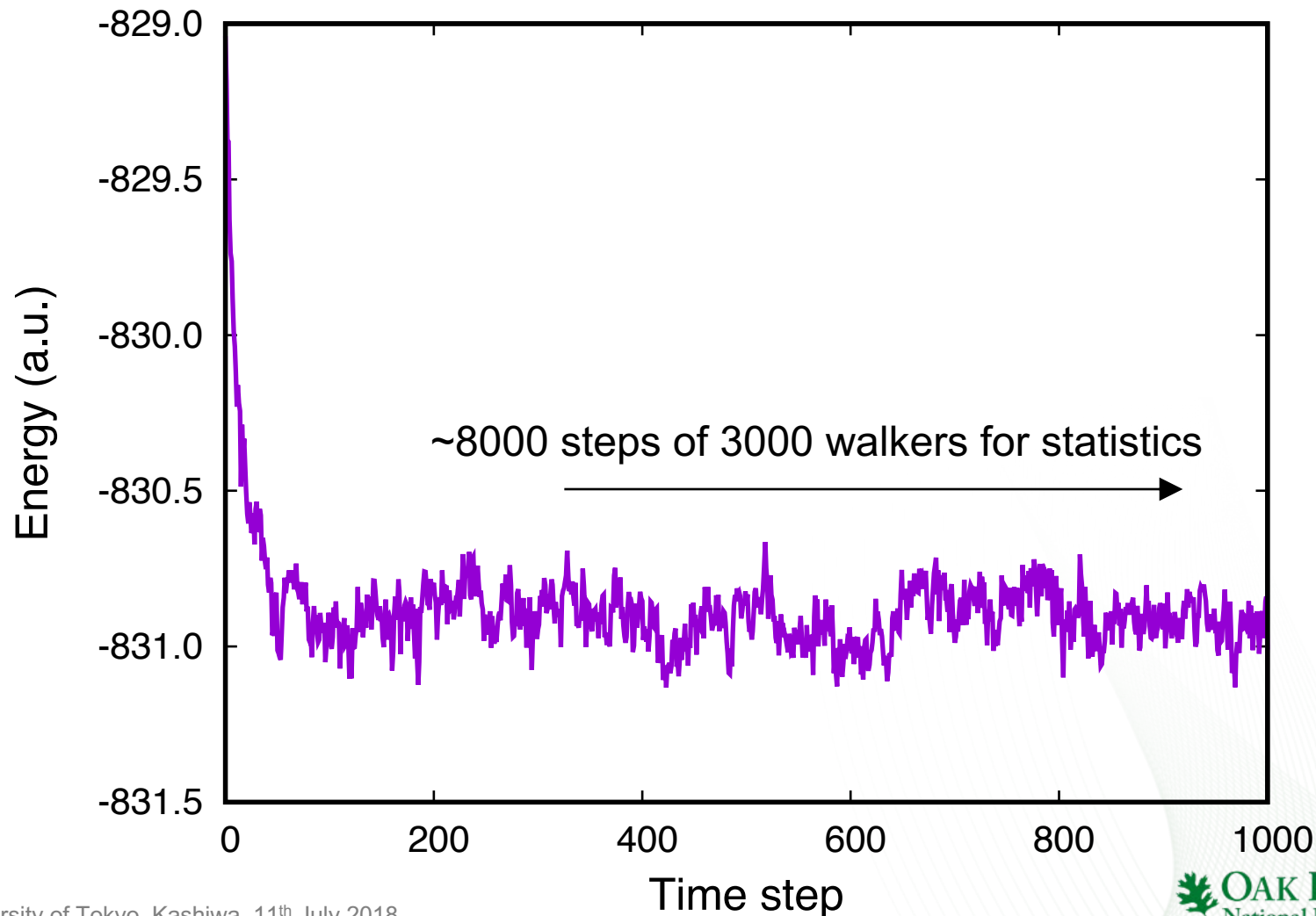


After initial projection to ground state, branching random walk has greatest density where wavefunction probability largest

Real Example: Bulk VO₂

Production run from Kylanpaa PRM 1 065408 (2017).

200 electrons, 0.01 a.u. timesteps



Key features of DMC

Advantages

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

Easily take advantages of supercomputers.

Becomes faster, cheaper with improved trial wavefunctions.

Disadvantages

Cost in solid-state! Have to take statistics in large enough cells.

Small timestep needed for high Z .

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

Errors, Limitations, Approximations

Potentially all controllable

“Fixed node”: Variational error in energy.

Large supercells/finite size scaling needed for periodic systems.

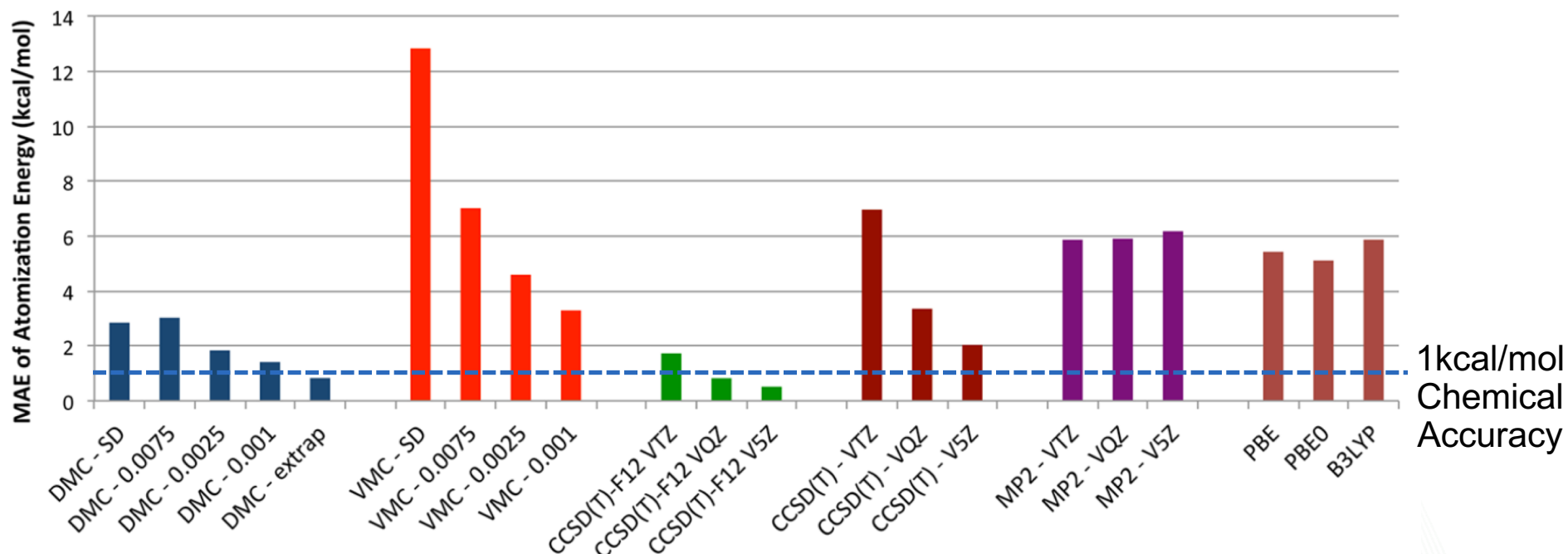
Outline

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- **Examples of today's capabilities**
- Future directions. Speculative!

Molecules / isolated systems

Chemical accuracy of <1 kcal/mol achieved using the “linear method” for VMC optimization of Umrigar et al. PRL (2007).

Trial wavefunctions use large multideterminant expansions (not widely possible in solids yet). DMC better than VMC.

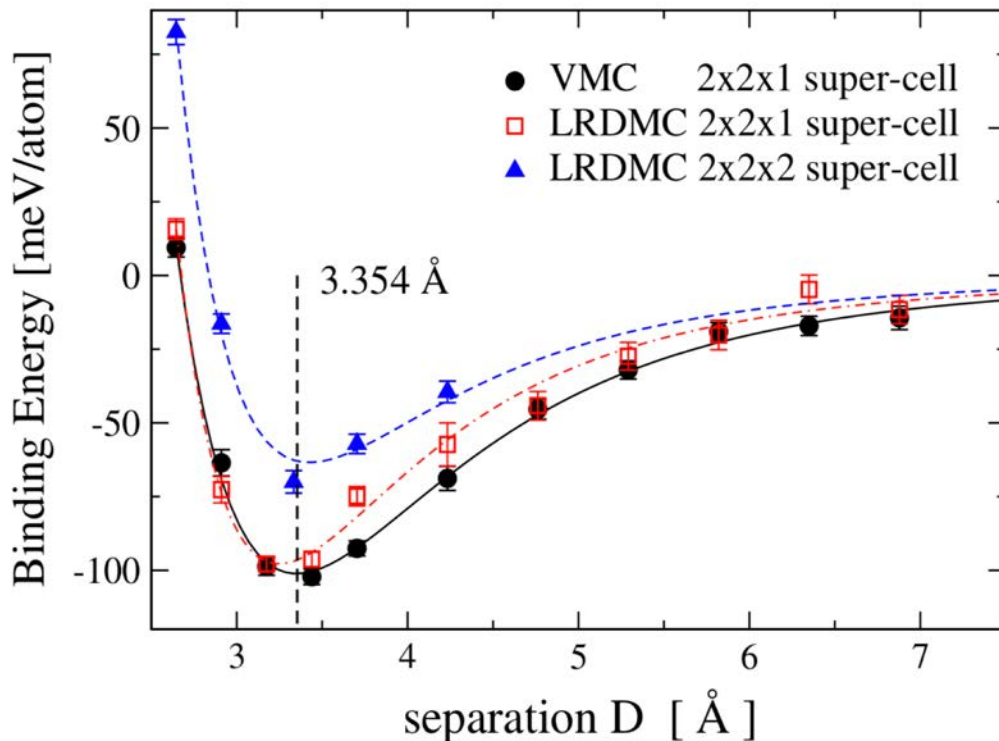


G1 test set. Morales et al. JCTC 8 2181 (2012)

VdW Review: M. Dubecky Chem. Rev. 116 5188 (2016)

Solids: Graphite & Van de Waals

- Graphite (A-B stacked graphene sheets) is bound via weak Van de Waals forces. Long a challenge for DFT.
- Accurate treatment of Van de Waals critical for the increasing number of 2D materials, 2D heterostructures.



DMC calculations with up to 64 atoms, 256 electrons.

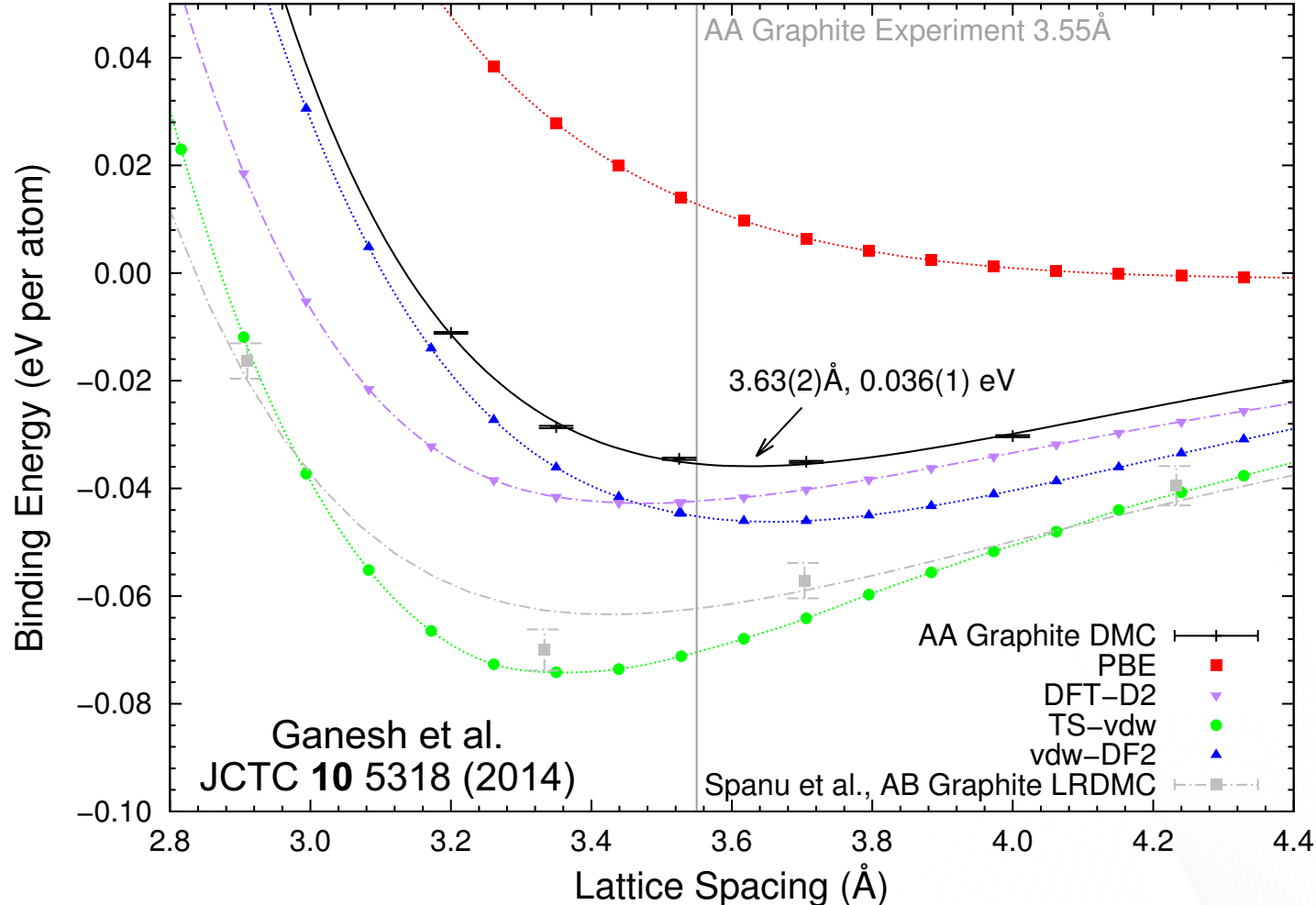
Simple, single determinant trial wavefunctions from DFT.

Predicted binding energy (56 meV/atom) close to experiment (62 meV/atom), lattice parameter within 2%.

Now well predicted by various Van de Waals DFT methods.

L. Spanu, S. Sorella, G. Galli PRL **103** 196401 (2009)

QMC for A-A Graphite Helps Identify Preferred VdW DFTs



- DMC is within 0.1Å of experiment. A-A stacked graphite sensibly higher in energy than A-B stacked ground state.
- Self-consistent VdW functionals perform best in this case.

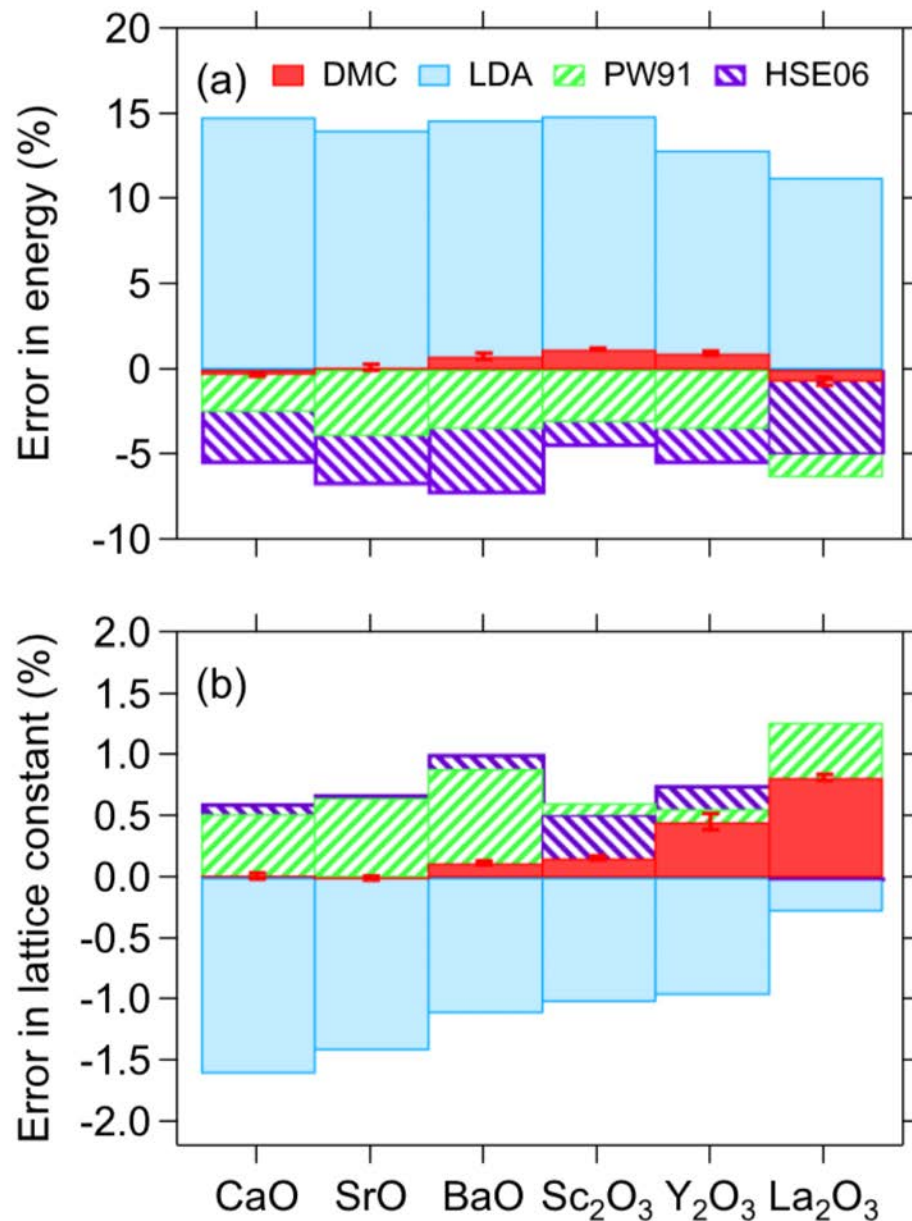
Solids: Metal oxides

Single determinant DMC results are the most accurate in cohesive energy and lattice constant.

Error increases for heavier elements.

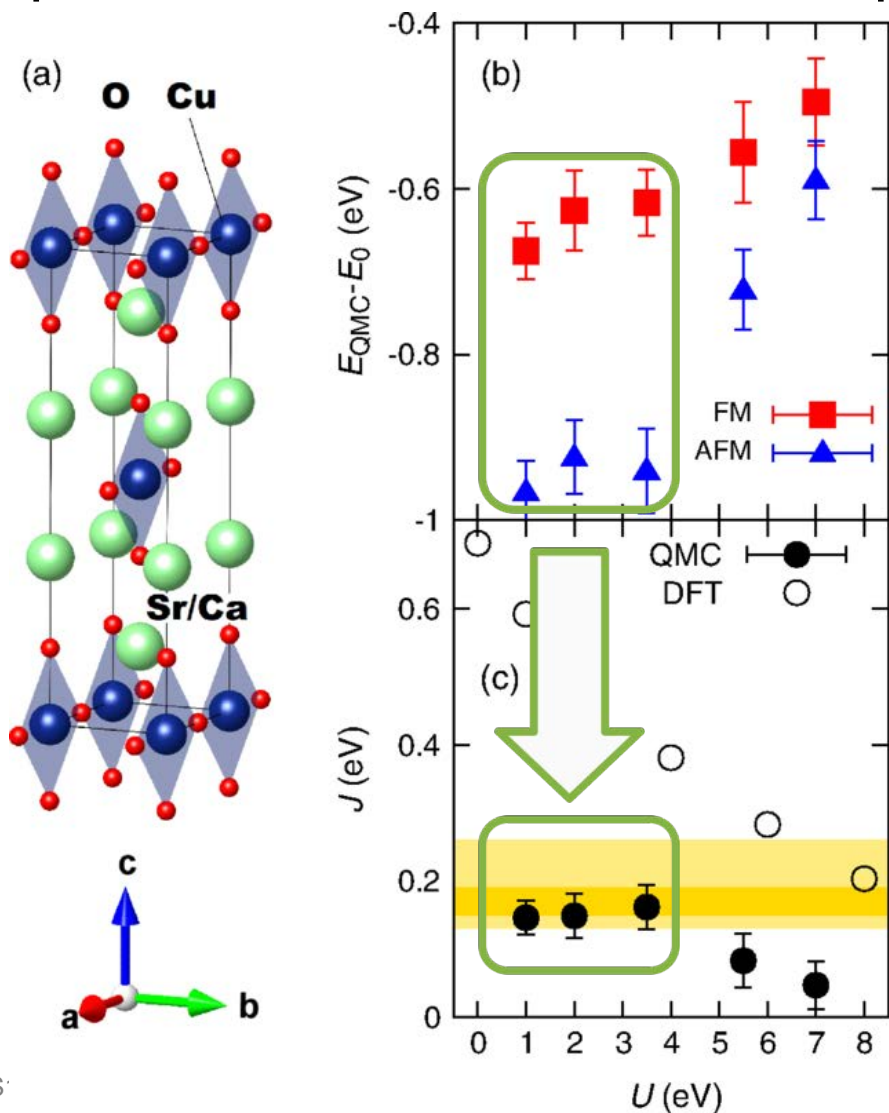
Recall: These are **not** exact calculations. Relative size of nodal and pseudopotential errors is not known.

J. Santana et al. JCP (2016,2017)



Copper oxides

The best variational DMC results give the best agreement with experiment. Note: DFT+U is simply not predictive.



Method	J (eV)
Experiment (INS)	0.241(11) Ref. [12]
Experiment [$\chi(T)$]	0.146(13) Refs. [7,13]
	0.189(17) Ref. [8]
FP DMC	0.159(14) This work
	0.115(10) This work [14]
Cluster DDCI3	0.231 Ref. [10]
UHF	0.04 Ref. [10]
LDA	0.64 This work

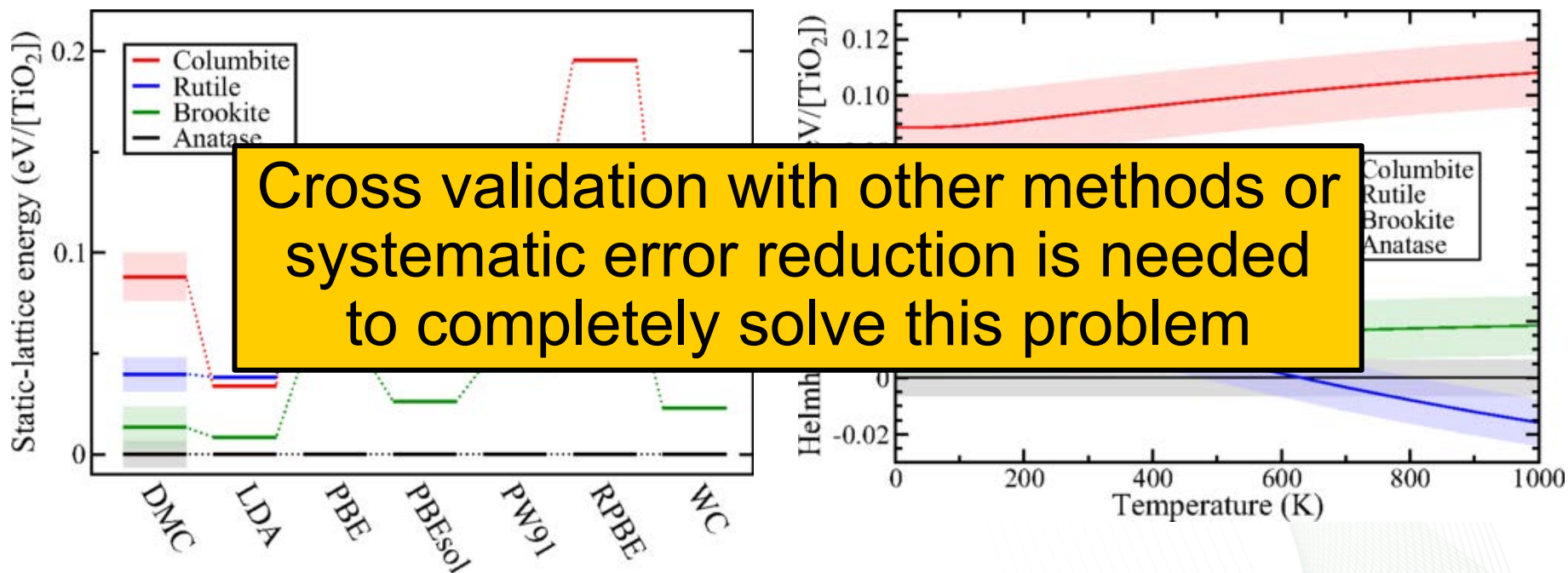
K. Foyevtsova et al.
PRX 4 031003 (2014)

Expt.

Other studies inc. La_2CuO_4 :
L. Wagner et al. PRB 90 125129
(2014), PRB 92 161116 (2015)

The Titania (TiO_2) Conundrum

- Rutile generally considered to be stable phase at ambient.
- Most DFTs at 0K **find anatase most stable**, famously claimed to be an error.
- Two QMC results (different codes, choices) also **find anatase most stable** at 0K. Finite T vibrational contributions to stability are important (via DFT).
- A few million CPU hours cost

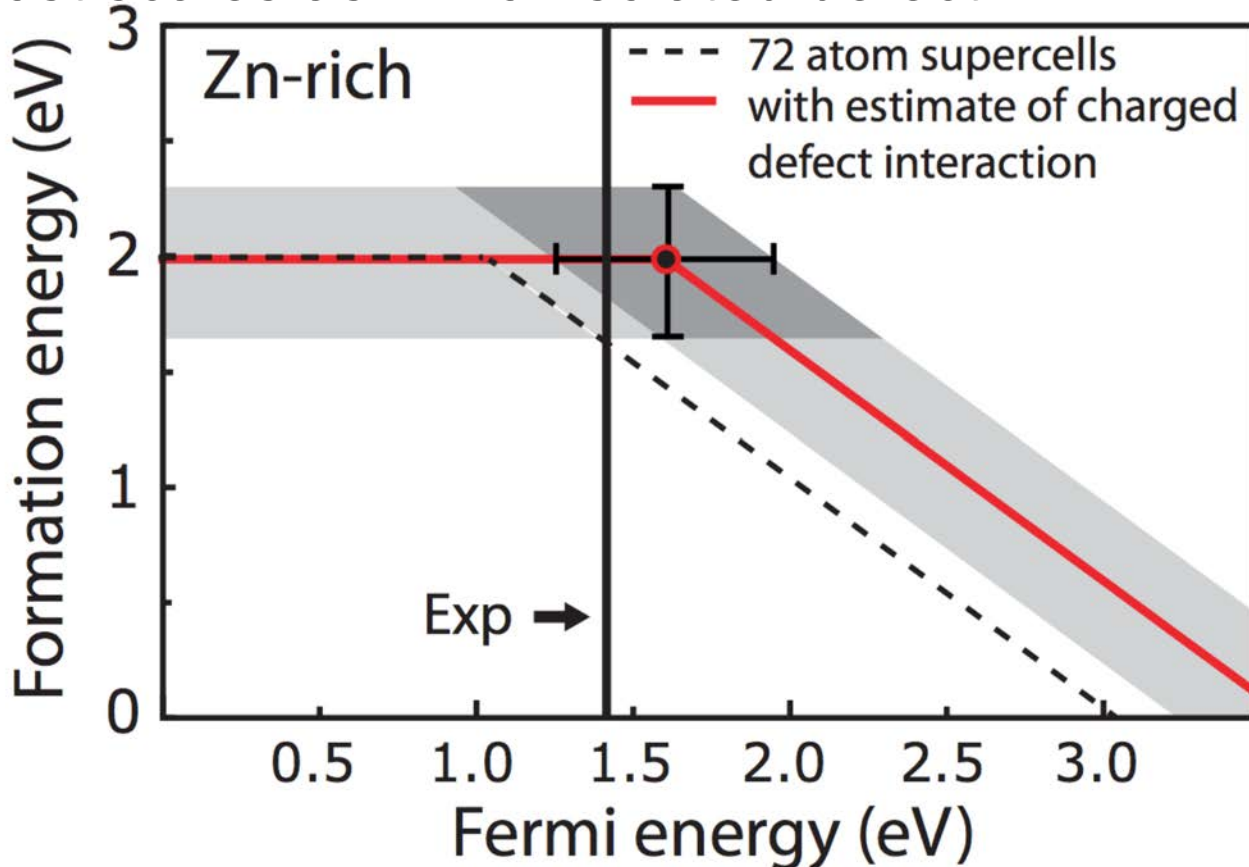


Cross validation with other methods or systematic error reduction is needed to completely solve this problem

J. Trail et al. PRB **95** 121108 (2017), Y. Luo et al. NJP **18** 113049 (2016)

Nitrogen defects in Zinc Oxide

Use supercell methods and charged defect corrections similar to DFT. Cost scales as N^4 for isolated defect.



Yu et al. PRB **95** 07209 (2017)

Includes thorough discussion & assessment of errors:
supercell size, nodal error, geometries, pseudopotentials, ...

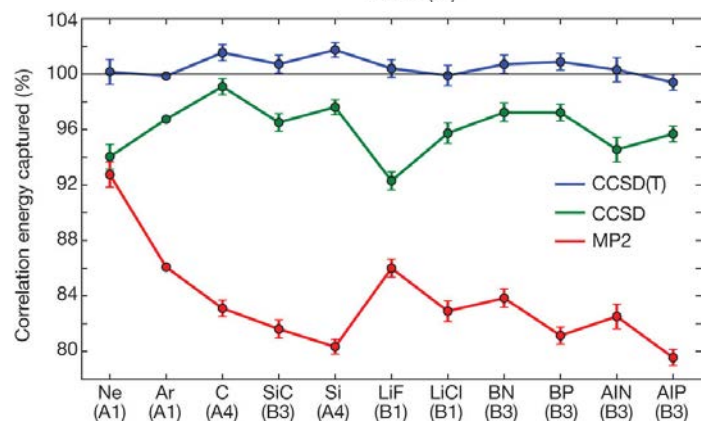
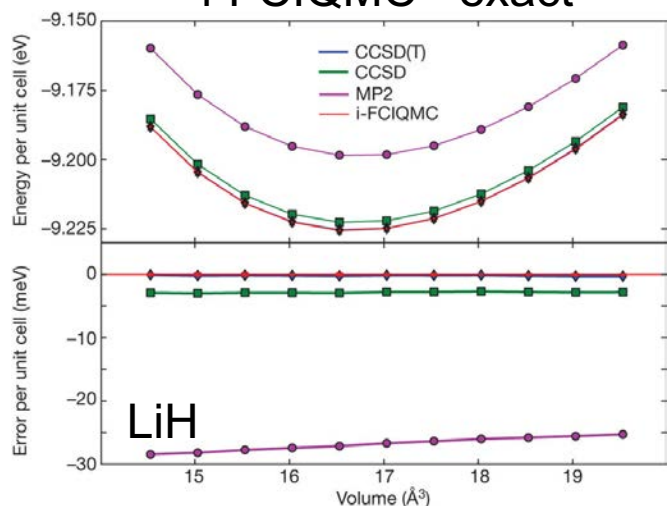
Outline

- Motivation
- Introduction to QMC methods
- Examples of today's capabilities
- **Future directions.**
 - Combining/comparing multiple methods
 - HPC
 - Informing DFT

Determinantal & Orbital-based QMC

The previous DMC calculations are still not exact. Improvements and cross-validation with other methods is needed.

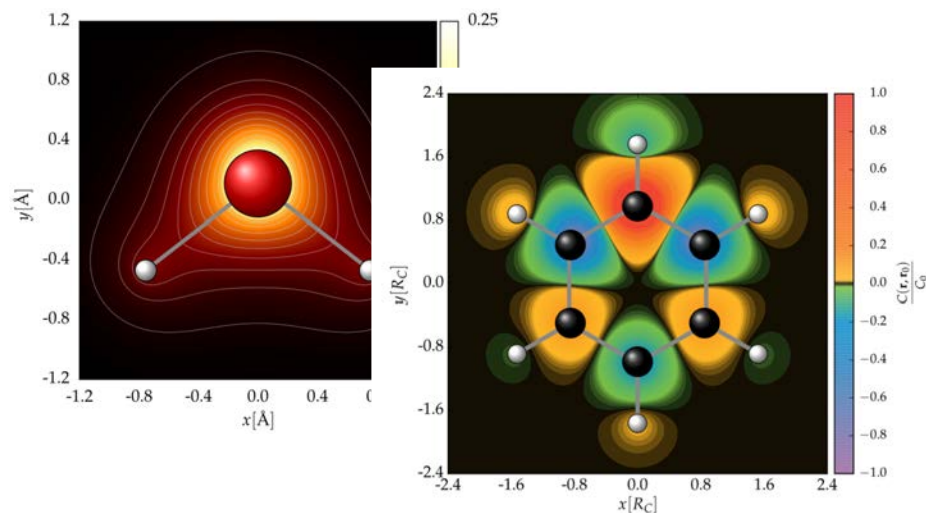
FCIQMC for solids (& CCSD(T)) i-FCIQMC ~exact



G. Booth et al. Nature **493** 365 (2013)

Auxiliary Field QMC

Based on Hubbard-Stratonovich transform of H



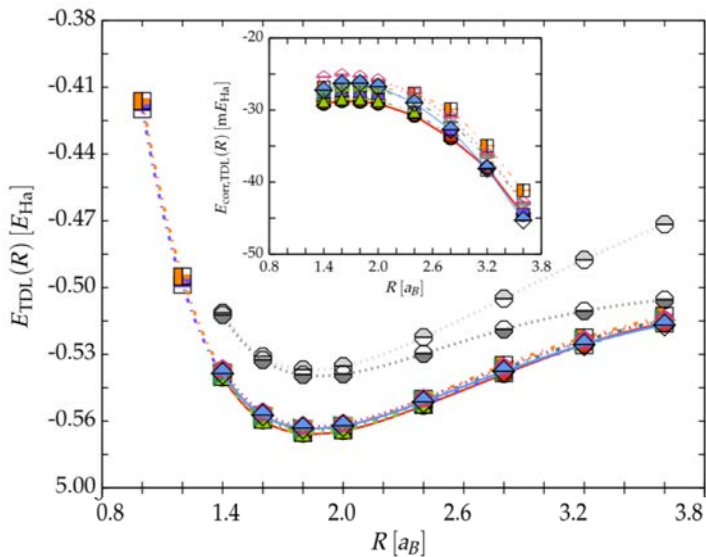
M. Motta & S. Zhang arXiv:1707.02684 and
Many prior results on solids, atoms, models...

Both methods allow for frozen core or multiple projector pp approaches, & easier computation of some observables than DMC.

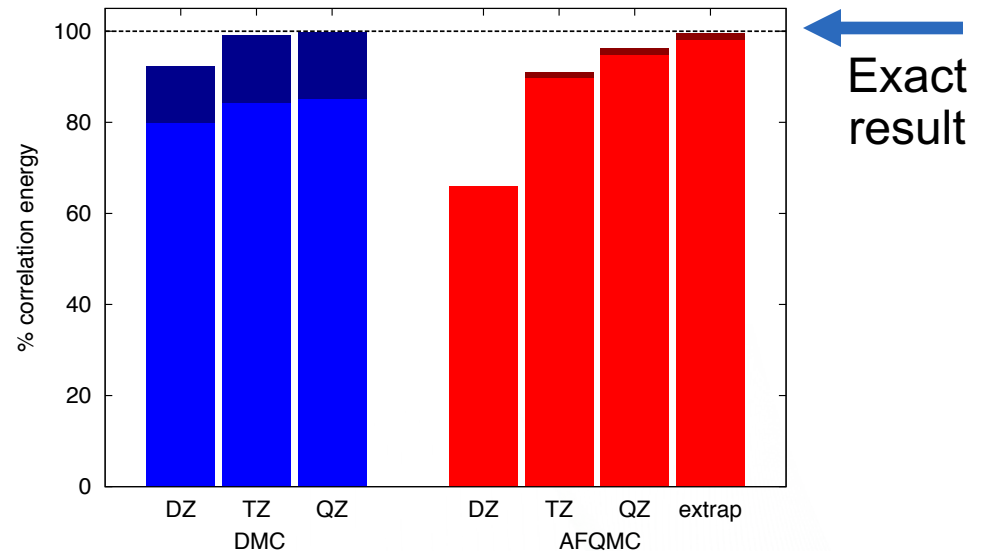
We have added an open source AFQMC to QMCPACK to enable cross-validation.

Cross-validation

Use of multiple, distinct methods will give stronger predictions and help drive methods improvement for strongly correlated materials. Possible for some model Hamiltonians and small molecules today, but not yet general materials.



H_{10} chain
 Many methods :
 DMC, AFQMC, DMRG,...
 Motta PRX 2017



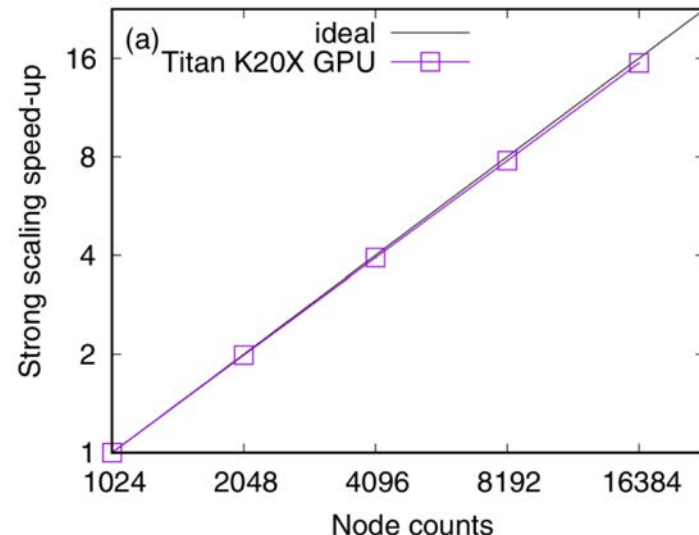
Carbon diamond primitive cell
 Multideterminants, large basis sets in DMC
 Strong basis set dependence in AFQMC
 Unpublished, M. Morales & A. Benali.

Advances in computation

- QMC algorithms use little communication: they scale from the desktop to the largest supercomputer.
- Smaller error bars, larger supercells, more electrons accessible with increased supercomputer power.
- Improved methods & algorithms always preferred!



QMCPACK runs well on Summit at Oak Ridge and should run well on upcoming A21, Frontier, Post-K...



Scaling to ~entirety of Titan machine at Oak Ridge
128 atom NiO, 1536 electrons

Improving DFT functionals?

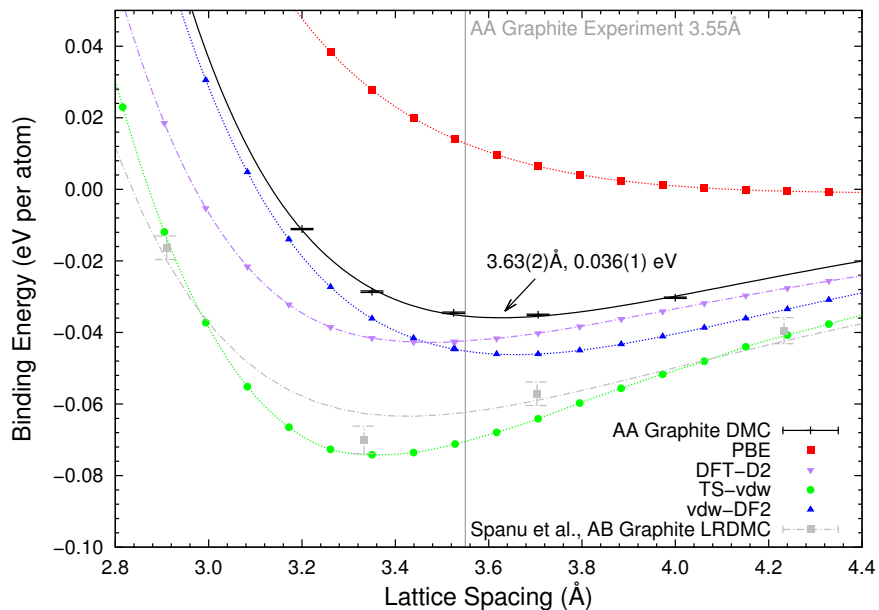
We are regularly asked “Can we use QMC to improve DFT functionals?”

Two components:

1. QMC data from real materials, models:
 - Choosing best functional for given application
 - Validating or training new functionals
 - Improved understanding from analyzing many-body wavefunctions
2. Choosing/constraining functional form of DFT approximation

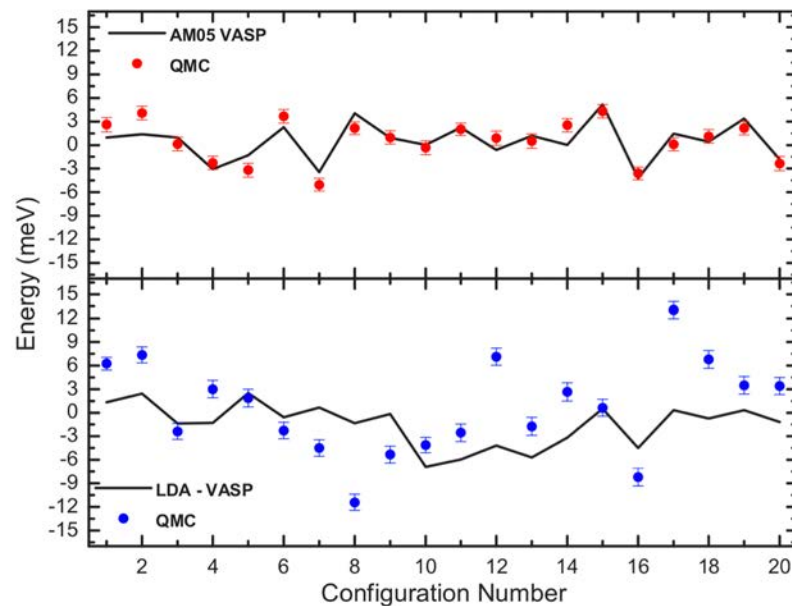
QMC can already inform DFT choice

Graphite, Lithium-Graphite
Pick best vdw method for more
extensive DFT studies



Ganesh et al.
JCTC **10** 5318 (2014)

Kr liquid at high pressure
AM05 has best agreement with QMC.
Use AM05 for large scale dynamics.

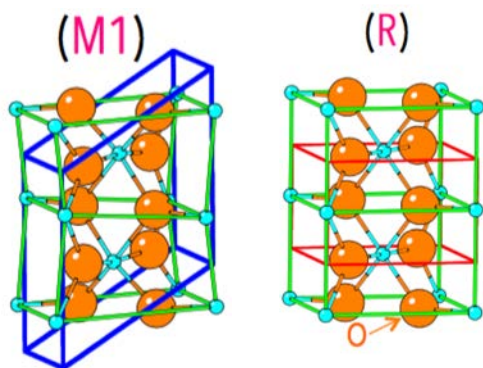


Mattsson et al.
PRB **90** 184105 (2014)

VO₂ metal-insulator transition and phase diagram

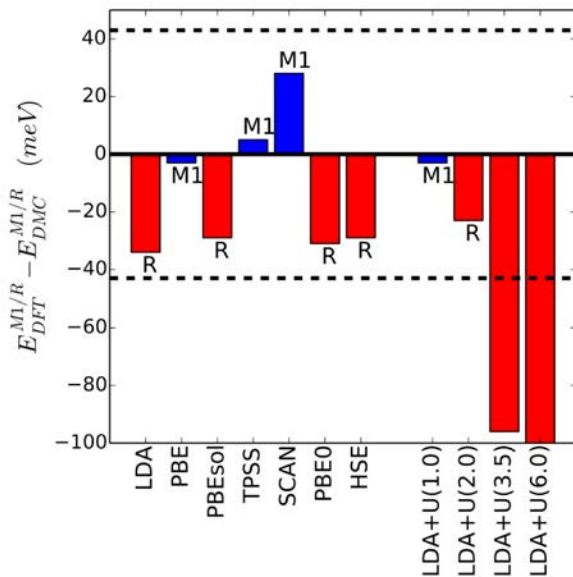
Long a challenge for "band theories" to obtain the correct phase ordering and physics. M1 transitions to rutile phase at ~340K, becoming metallic. Analysis of the QMC charge density -- with good statistics -- finds that functionals have difficulty with the vanadium d electrons (presumably self-interaction error.)

Structure

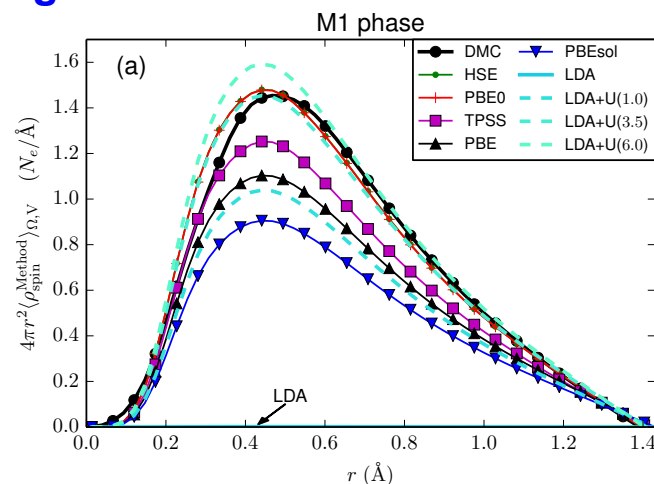


Phase stability

BLUE = Gives correct ordering



Spin-density analysis



I. Kylanpaa et al. PRM **1** 065408 (2017)

H. Zheng & L. K. Wagner PRL **114** 176401 (2015)

With access to energies and densities for many materials, we could empirically fit a functional or help design one. Similar to efforts in quantum chemistry. Important to include **many** physical constraints e.g. As per SCAN.

Analyzing the wavefunction

A better route to **understanding** successes & failures of DFT in both real materials and model systems could be analyzing the QMC wavefunction in more depth.

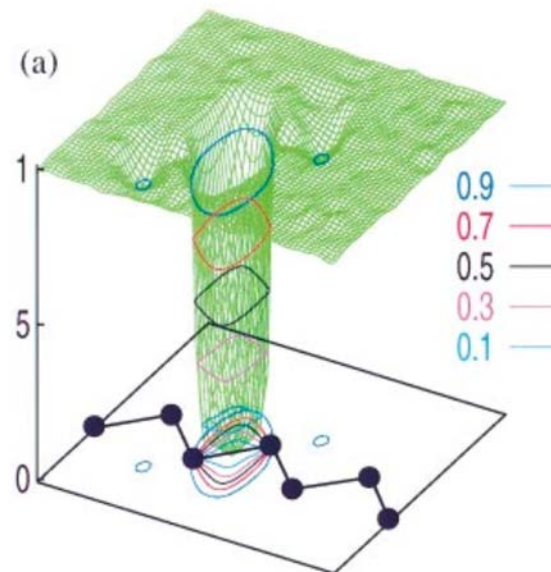
Accessible quantities: Density $n(\mathbf{r})$, pair correlation function $g(\mathbf{r}, \mathbf{r}')$, density matrix $n(\mathbf{r}, \mathbf{r}')$, exchange correlation energy density $e_{xc}(\mathbf{r}), \dots$

Little explored: bulk Si, some model and atomic systems.

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

Monte Carlo integral over N-2 particle positions + Coupling constant integration.

R. Q. Hood et al. PRL **78** 3350 (1997)



$g(\mathbf{r}, \mathbf{r}')$ spin parallel, one electron on bond center, Si (110) plane

Bulk silicon wavefunction analysis

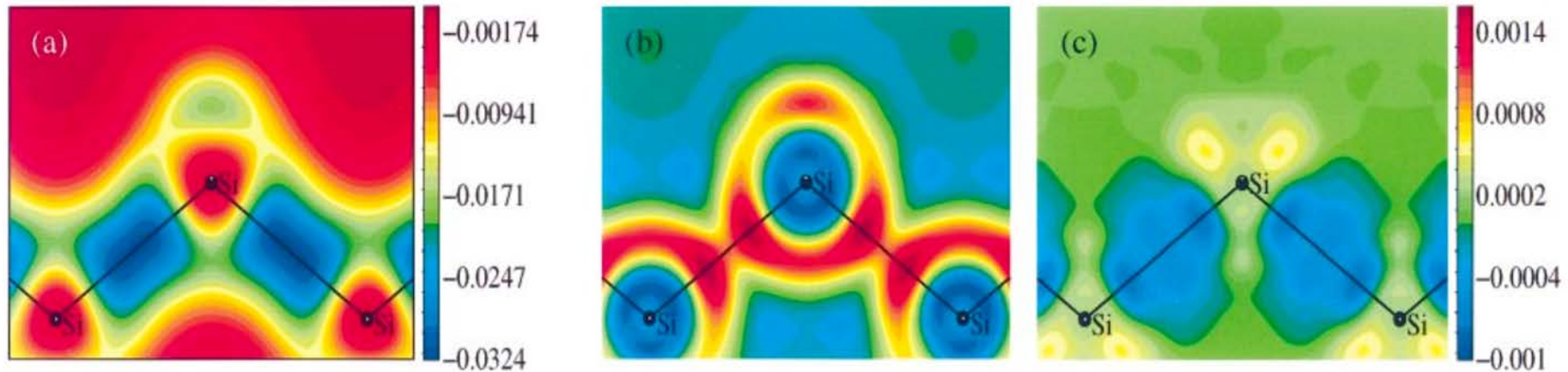


FIG. 4(color). Contour plots along the (110) plane for (a) $e_{xc}^{VMC}(\mathbf{r})$, (b) $e_{xc}^{VMC}(\mathbf{r}) - e_{xc}^{LDA}(\mathbf{r})$, and (c) $e_{xc}^{VMC}(\mathbf{r}) - e_{xc}^{ADA}(\mathbf{r})$. (b) and (c) have the same legend shown to the right of (c). The atoms and bonds are schematically represented for bond chains along the [111] direction.

ADA (averaged density approximation) performs better than LDA in this case.

Some evidence of real space cancelation of errors in LDA

Datasets are very rich!

R. Q. Hood et al. PRL **78** 3350 (1997)

R. Q. Hood et al. PRB **57** 8972 (1998)

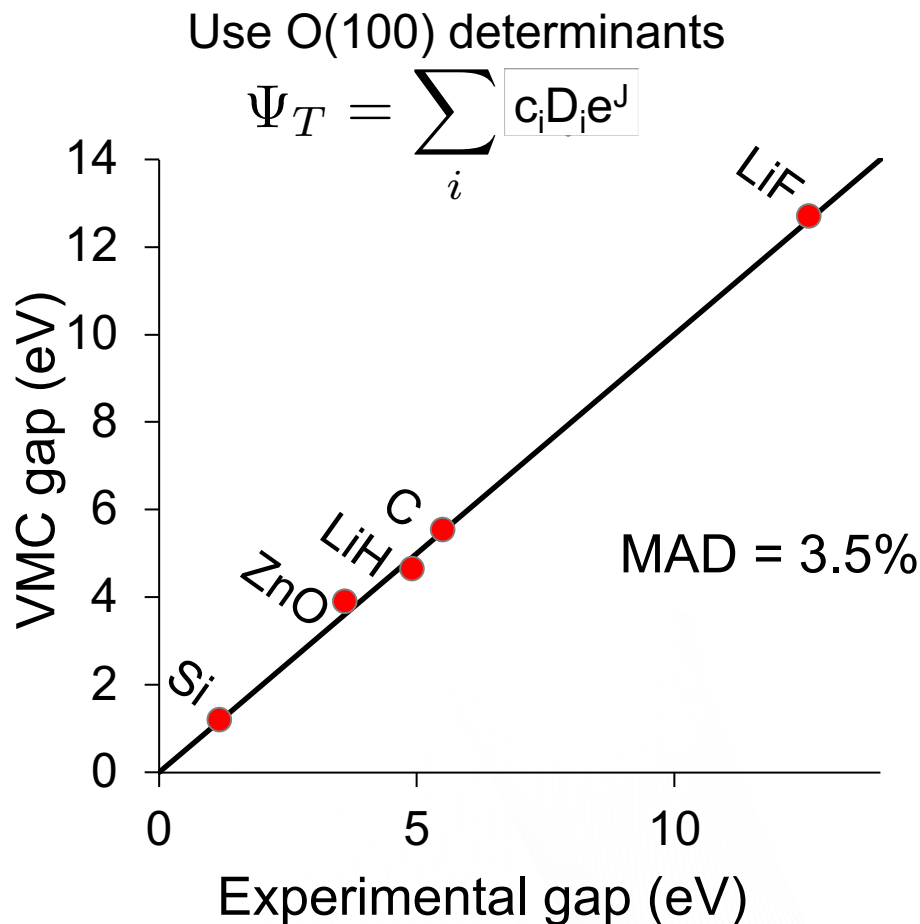
This analysis has not been repeated in other materials or modern functionals.

Summary: Informing DFT

- QMC can be used to help select the most accurate existing functional today. Similar to use of quantum chemistry for molecular systems.
- With access to energies and densities, improved functionals can potentially be created. Important to heed the lessons of Medvedev et al. *Science* (2017).
- Difficult in general – a focused approach is most likely to be successful.
- Analysis of wavefunctions may yield better understanding.

Towards Accurate Excited States

- Current QMC methods do not produce spectra: Excited states have to be computed one at a time
- Generally only the first state of each symmetry can be obtained in DMC
- Usually excited state wavefunctions are worse than for ground state.
- New VMC technique for optimization of excited states improves accuracy.



L. Zhao and E. Neuscamman
Submitted to PRL

J. Shea and E. Neuscamman
JCTC **13** 6078 (2017)

Conclusions

- Stochastic methods are a promising route to meeting the challenge of the full quantum many-body problem.
- Today, QMC can to be applied to important materials where DFT approximations are questioned.
- Accurate wavefunctions from QMC in solids can potentially inform DFT approximations and other theories.

kentpr@ornl.gov

QMCPACK

www.qmcpack.org