Ab initio Quantum Monte Carlo

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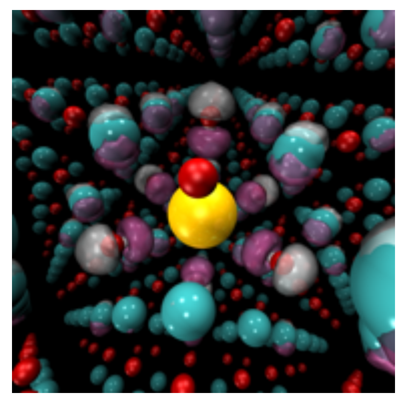


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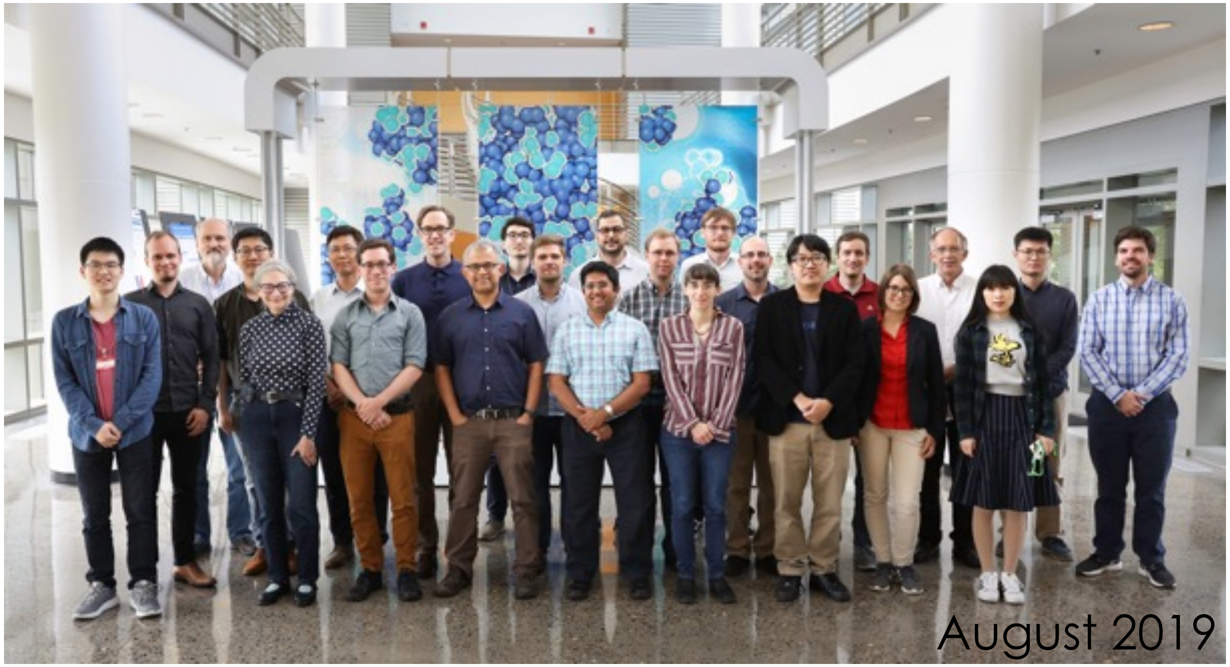
Acknowledgments

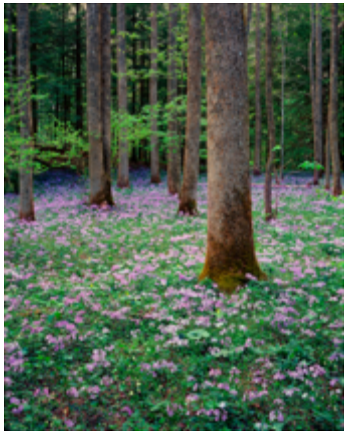


- Members of Center for Predictive Simulation of Functional Materials, from Livermore, Sandia, Argonne, Oak Ridge Labs, UC Berkeley, Brown, & North Carolina State U.
- While focused on QMC and open source QMCPACK, we also do DFT, DMFT, GW and experimental validation.
- INCITE supercomputer time.

QMCPACK

We are hiring – talk/email/apply ASAP if interested

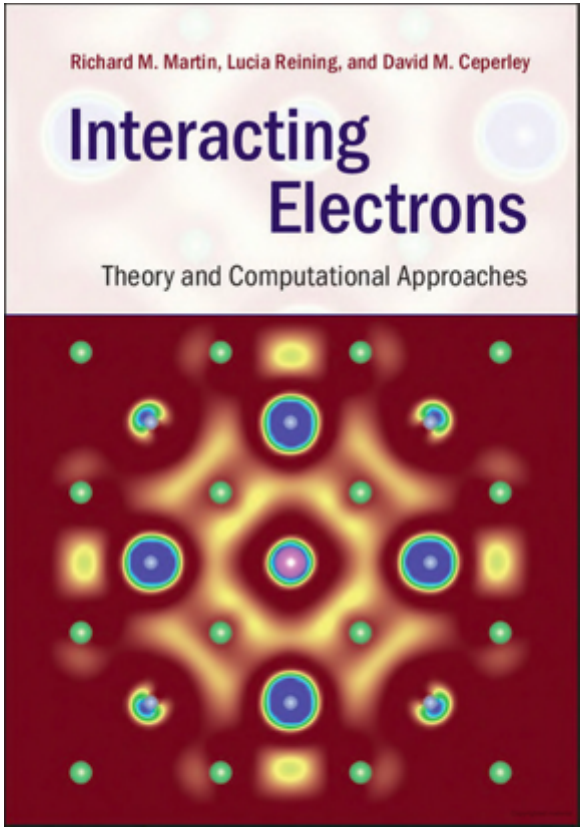
- Staff scientist in computational many-body theory
  - Interested in all post-DFT methods: GW, DMFT, QMC,…
- Post-doc in Quantum Monte Carlo (Reboredo)
- Distinguished Fellowships
  - "Named postdocs" often leading to a staff position
- Post-doc in first-principles calculations for MXenes
  - Strong experimental collaborations

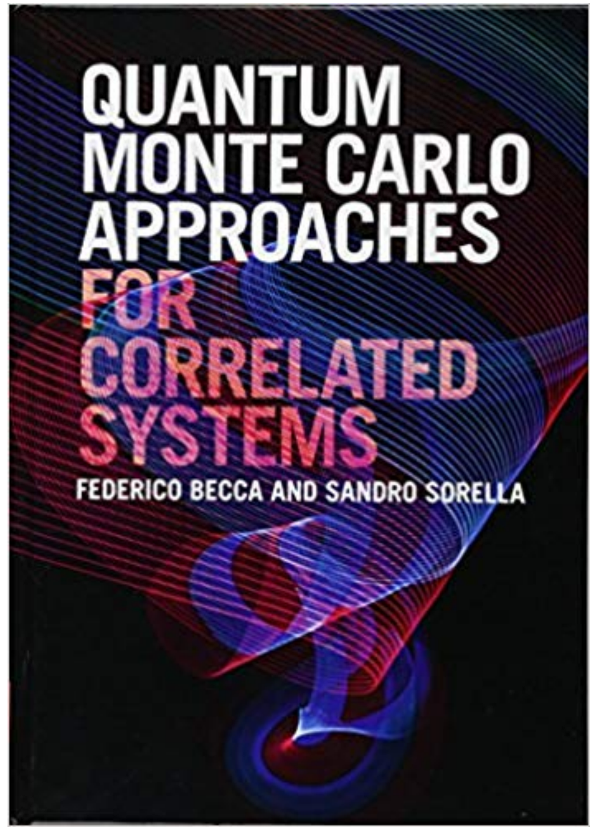



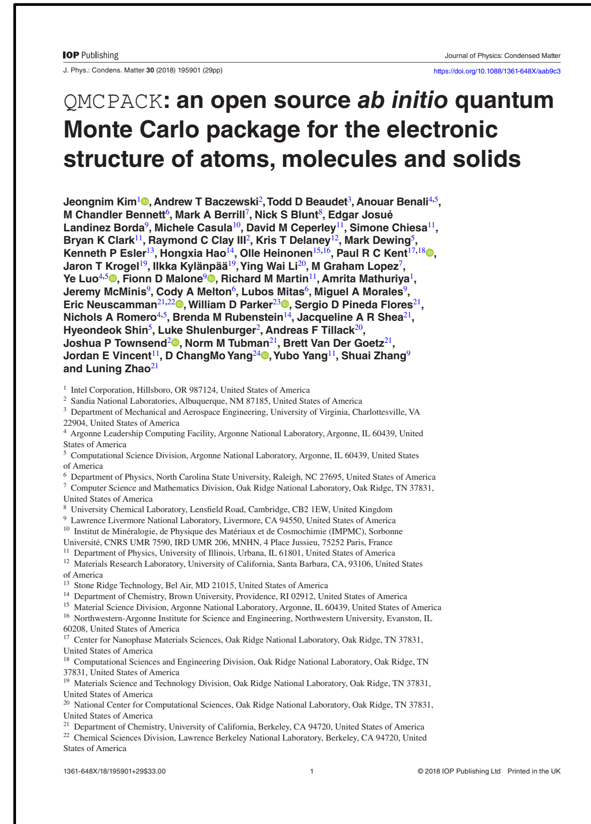

Outline

- Motivation and Introduction
  - Why take on an NP hard problem?
  - What is achieved today?
  - Why is the field growing?
- Quantum Monte Carlo Methods
  - There are many; Details matter
  - Real-space VMC, DMC, orbital space AFQMC
- The Future
  - New capabilities
  - New (& old) connections between QMC, GW, DMFT, DFT.

To find out more







IOP Publishing Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter **30** (2018) 195901 (29pp) https://doi.org/10.1088/1361-648X/aab9c3

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) [real space only, older]
QMCPACK citation: J. Kim et al, JPCM **30** 195901 (2018) [newer references, methods]

Our Challenge

Solve the many-body Schrodinger equation for general systems and with only readily controllable approximations

Our Goals

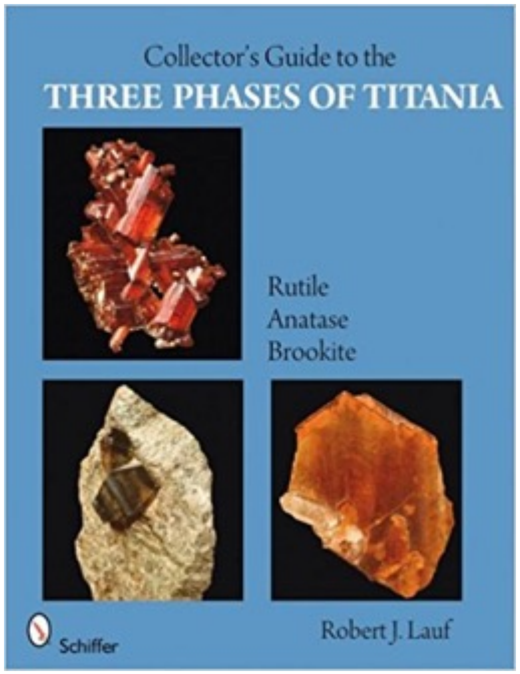
Develop a practical and convergent method for real materials and chemistry

Understand many-body physics, chemistry, materials

Provide useful benchmarks and make connections to other methods, particularly for periodic systems, and eventual upscaling

Collaboration wanted: Experiment can't provide all the answers we need or are asked to provide

No Definitive Result

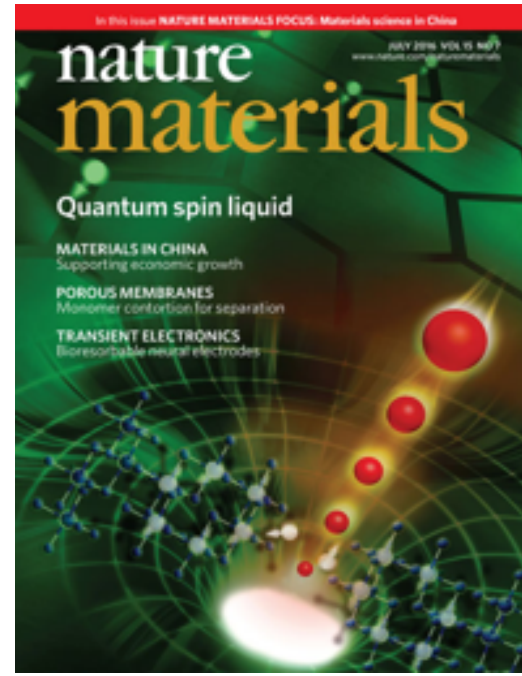


TiO_2 shows multiple metastable phases. Different theory and experimental camps have argued which is the ground state.

New materials

MXenes (Prototype: Ti_3C_2), the largest family of 2D nanomaterials. Robust predictions needed to guide synthesis.

New phenomena

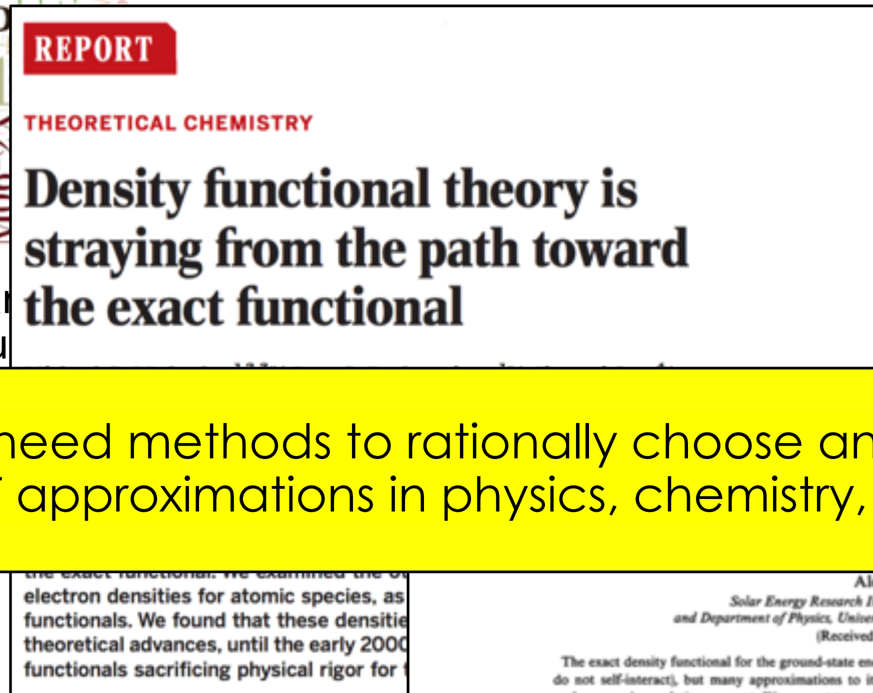


Neutrons show α-$RuCl_3$ "is close" to Kitaev quantum spin liquid. Models for QSL depend strongly on Hamiltonian parameters.

DFT challenges…

Word cloud of "popular
marcelswart.eu

Many DFT ap
to choo

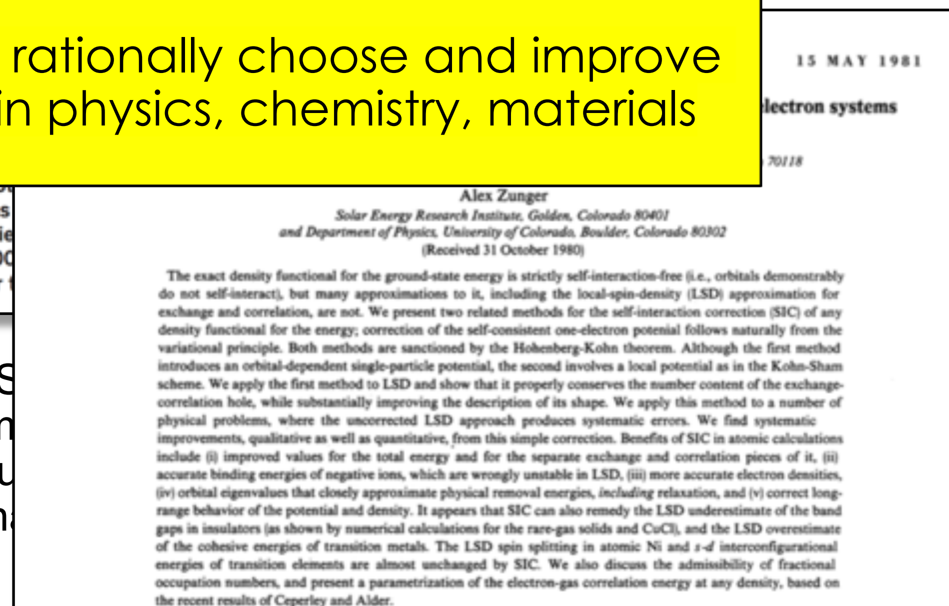


REPORT

THEORETICAL CHEMISTRY

Density functional theory is straying from the path toward the exact functional

electron densities for atomic species, as
functionals. We found that these densitie
theoretical advances, until the early 2000
functionals sacrificing physical rigor for



15 MAY 1981

lectron systems

70118

Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401
and Department of Physics, University of Colorado, Boulder, Colorado 80302
(Received 31 October 1980)

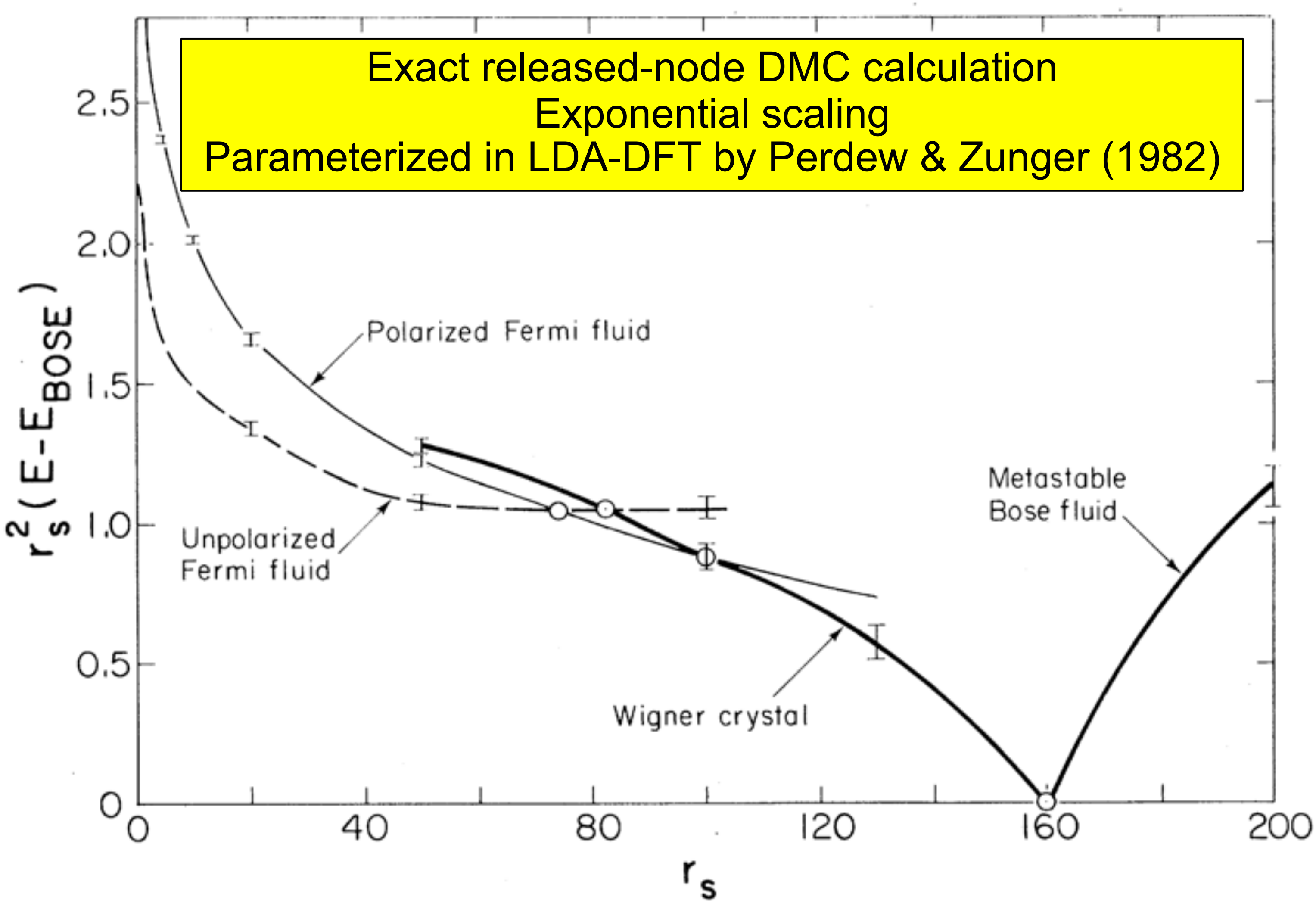
The exact density functional for the ground-state energy is strictly self-interaction-free (i.e., orbitals demonstrably do not self-interact), but many approximations to it, including the local-spin-density (LSD) approximation for exchange and correlation, are not. We present two related methods for the self-interaction correction (SIC) of any density functional for the energy; correction of the self-consistent one-electron potenial follows naturally from the variational principle. Both methods are sanctioned by the Hohenberg-Kohn theorem. Although the first method introduces an orbital-dependent single-particle potential, the second involves a local potential as in the Kohn-Sham scheme. We apply the first method to LSD and show that it properly conserves the number content of the exchange-correlation hole, while substantially improving the description of its shape. We apply this method to a number of physical problems, where the uncorrected LSD approach produces systematic errors. We find systematic improvements, qualitative as well as quantitative, from this simple correction. Benefits of SIC in atomic calculations include (i) improved values for the total energy and for the separate exchange and correlation pieces of it, (ii) accurate binding energies of negative ions, which are wrongly unstable in LSD, (iii) more accurate electron densities, (iv) orbital eigenvalues that closely approximate physical removal energies, *including* relaxation, and (v) correct long-range behavior of the potential and density. It appears that SIC can also remedy the LSD underestimate of the band gaps in insulators (as shown by numerical calculations for the rare-gas solids and CuCl), and the LSD overestimate of the cohesive energies of transition metals. The LSD spin splitting in atomic Ni and *s-d* interconfigurational energies of transition elements are almost unchanged by SIC. We also discuss the admissibility of fractional occupation numbers, and present a parametrization of the electron-gas correlation energy at any density, based on the recent results of Ceperley and Alder.

We need methods to rationally choose and improve DFT approximations in physics, chemistry, materials

Medvedev et al. S
+ comm
~ Energies & densities shou
Empirical fitting ha

Perdew & Zunger PRB **23** 5048 (1981)
The LDA DFT paper is about an error in LDA DFT
Most functionals still have self-interaction error
(really, delocalization error is key)

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

Mn Doped Phosphors with DMC

K. Saritas et al. JPCL **10** 67 (2019)

Excited states can be run

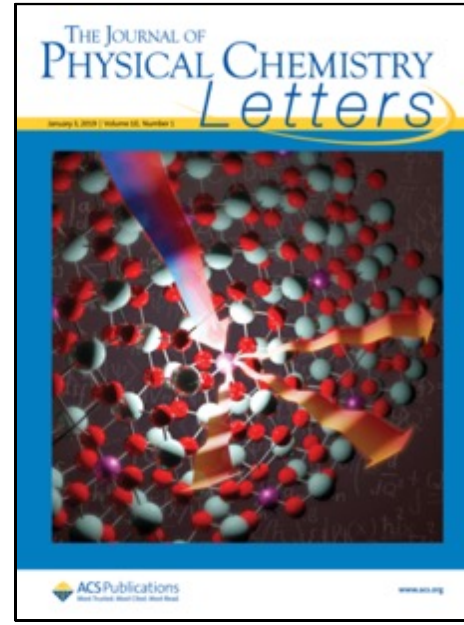
“Standard recipe” fixed-node single determinant DMC gives excellent results for emission energies vs experiment.

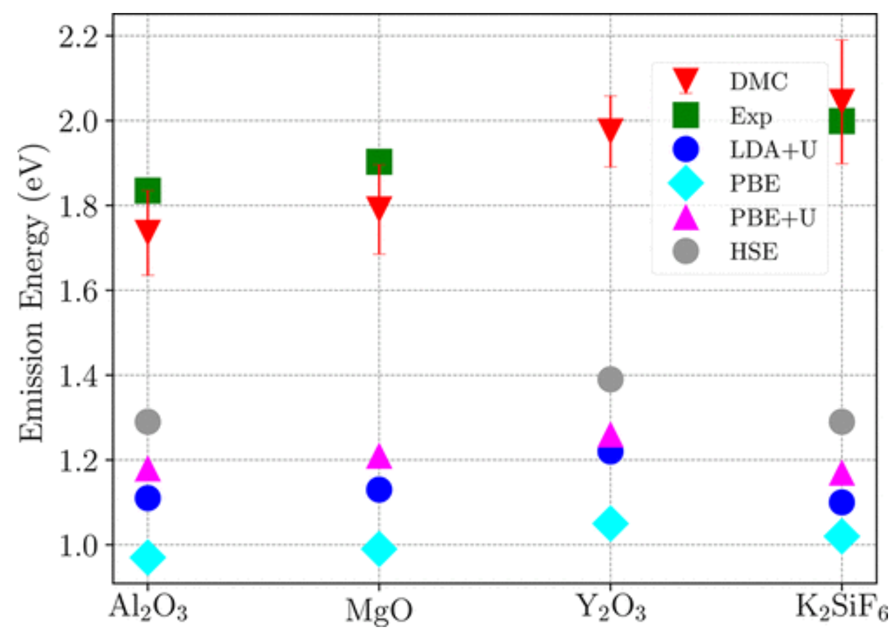
Predicts red Y_2O_3:Mn emission

Hybrid DFT is too low.

O(1M) CPU hours

No heroics.





Oak Ridge National Laboratory

Scandium oxide polymorphs

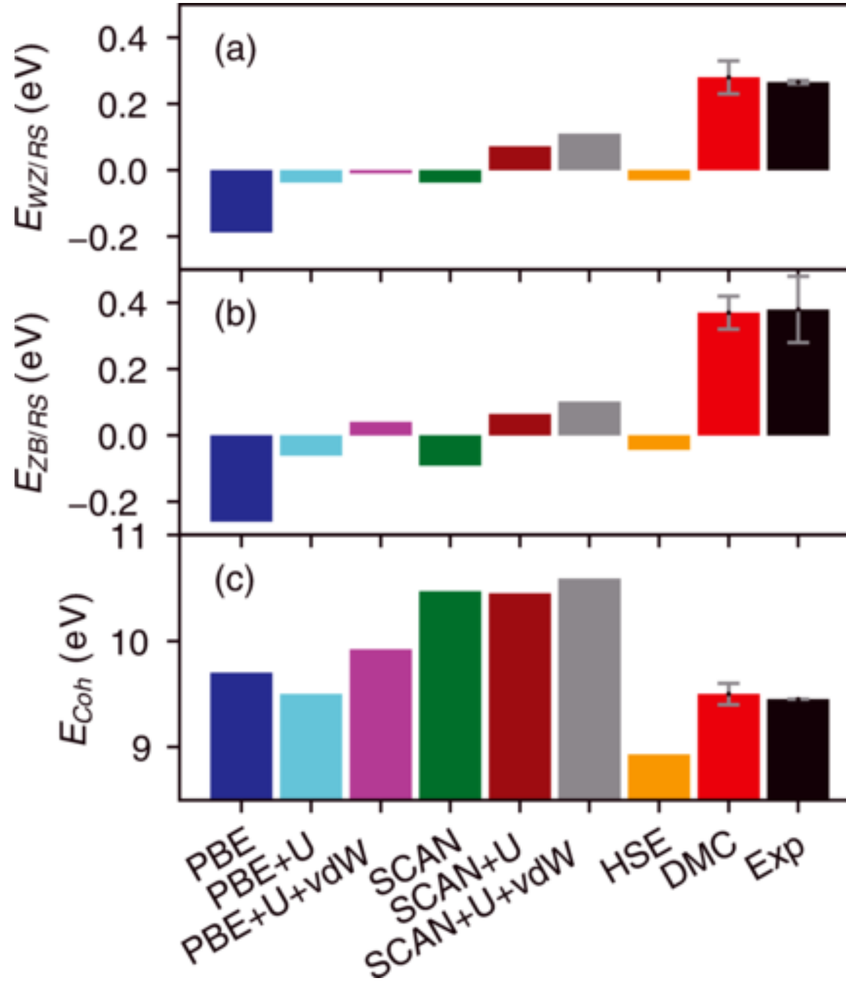
"Standard recipe" fixed-node single determinant DMC gives good thermodynamics, bulk moduli and correct energy ordering for **rocksalt**, **wurtzite**, **zinc blende**.

PBE, HSE, SCAN do not.

SCAN+U corrects order but overbinds.

Followed QMC workshop recipe.

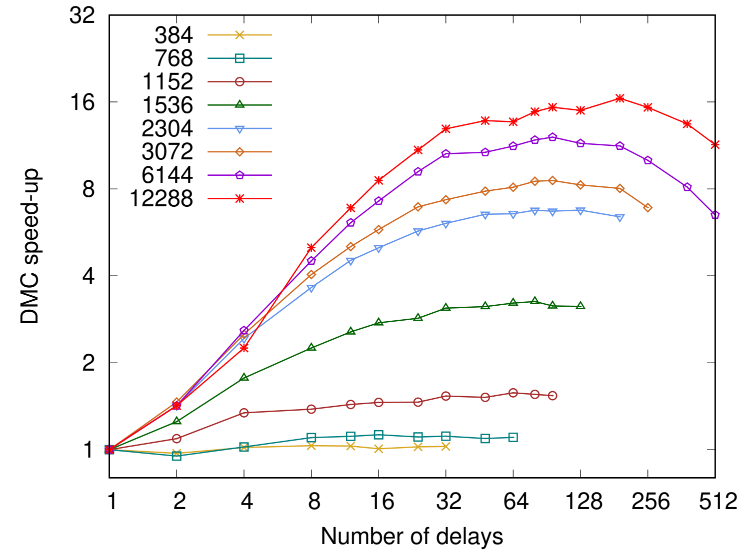
Setup for a later series of perovskite calculations with defects.



K. Saritas et al. PRB **98** 155130 (2018)

Why the Field of QMC is Growing

"Delayed update" algorithm



Massive growth in computing increases accessible materials

- Accelerated computation (GPUs & more) driven by power efficiency
- Memory size & type
- Institutional level resources are very useable.

New ideas, methods, algorithms

- New methods including AFQMC, FCIQMC…
- Numerics: QMC is 2-10x faster for solids than ~2 years ago
- New related methods: Stochastic GW, CC…

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  - Real-space VMC, DMC, orbital space AFQMC
- The Future
  - New capabilities
  - New (& old) connections between QMC, GW, DMFT, DFT.

Monte Carlo Methods

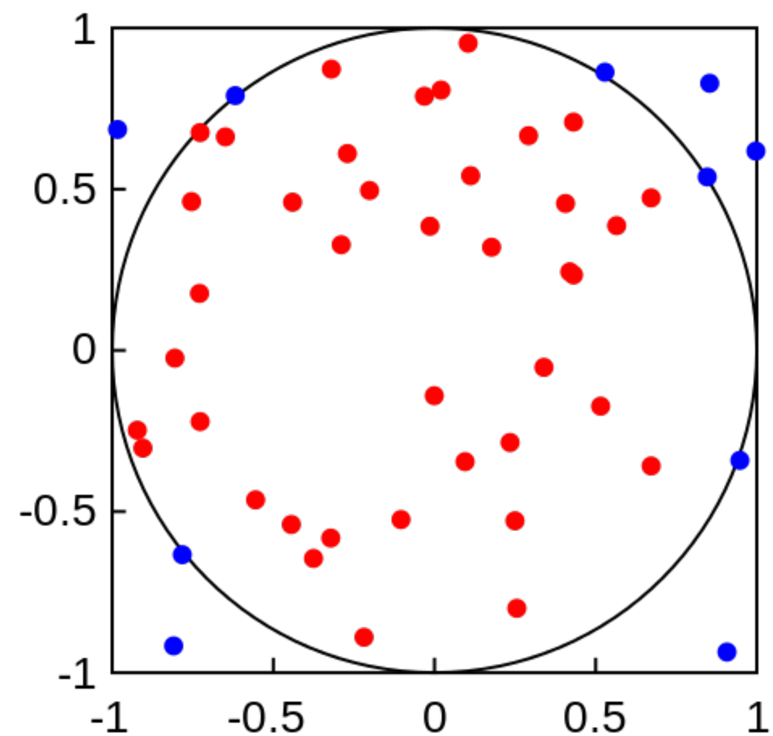
Use statistical methods to tackle the high dimensionality of the Schrodinger equation: Monte Carlo is more efficient than numerical integration in high dimensions.

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

Estimate π 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 !
Sample accurately (importance sampling)
Plan calculations carefully!



Wikipedia

Flavors of Ab initio Quantum Monte Carlo

All can treat strong electronic correlations, Van der Waals etc.

- Real space QMC
  - Sample electron positions in real space
  - Variational, diffusion, reptation…
  - Longest established, most results
- Auxiliary Field QMC   Motta & Zhang Comp. Mol. Science **8** e1364 (2018)
  - 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 a basis of determinants
  - Potentially 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
Great flexibility: only need to evaluate value & derivatives in real space

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

Red-shaded part is a probability density: positive definite & normalized
Use textbook Metropolis Monte Carlo
For 1000 electrons = 3000 dimensional integral

Modern QMC trial wavefunctions

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

(1) Start with best affordable density functional or quantum chemistry wavefunction.
(2) Reoptimize some or all coefficients.

Parameterized **Jastrow factor**. **Build in physics**, e.g. wavefunction cusps. *Greatly* improves trial wavefunction. Does not change nodes

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

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

Molecules
State of art: O($10^{4\text{-}5}$) determinants
+ Jastrow and full reoptimization

Solids
Today mostly single determinant
from DFT+U/EXX + Jastrow

Other options: Backflow, Geminals…

Key features of VMC

Advantages	Disadvantages
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	Finite size scaling for periodic calculations 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

Project out ground state to minimize trial wavefunction dependence.

Write the time dependent Schrodinger equation in **imaginary time**

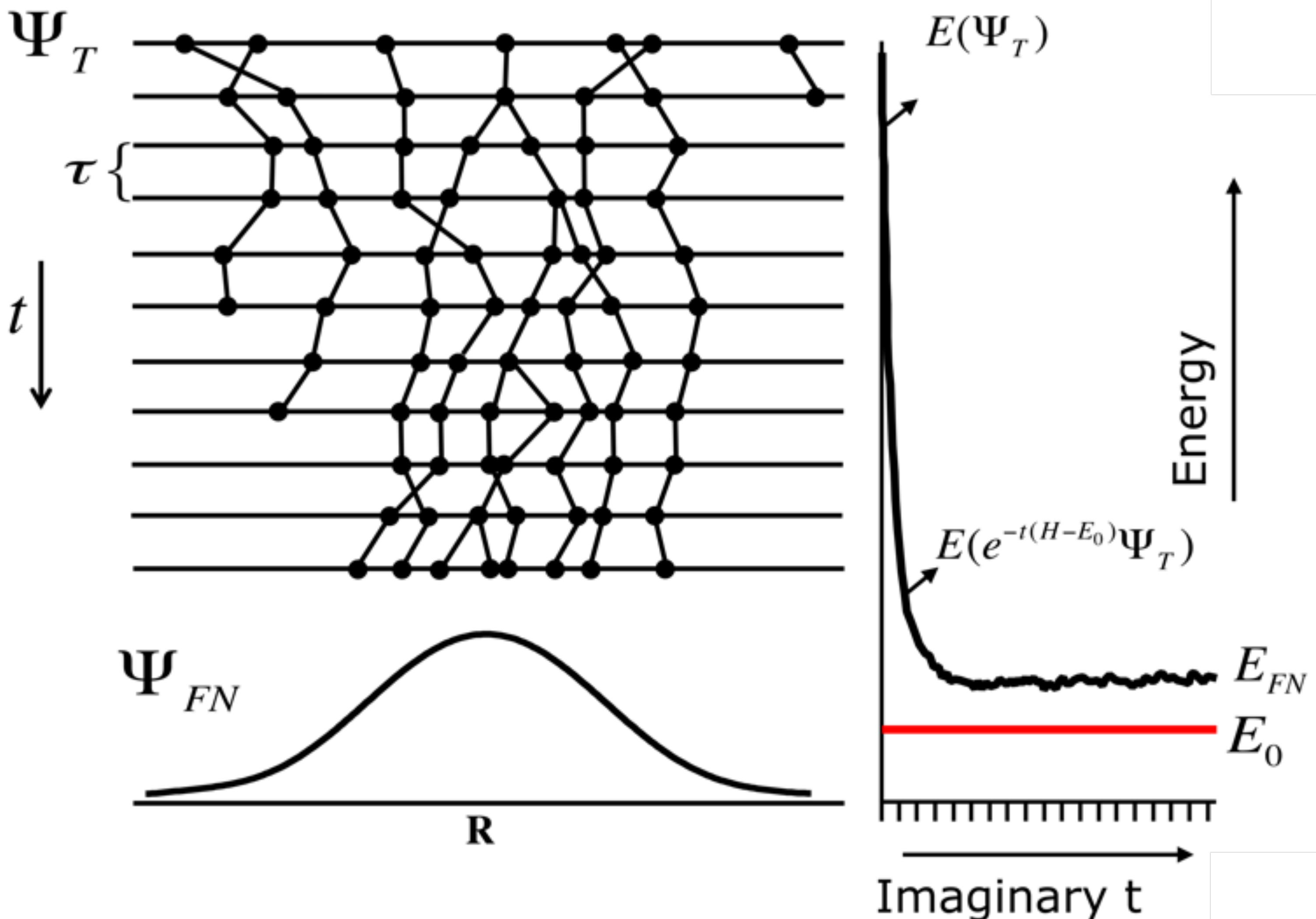
$$\frac{\partial|\psi\rangle}{\partial\tau} = -\hat{H}|\psi\rangle \qquad |\psi(\delta\tau)\rangle = \sum_{i=0}^{\infty} c_i e^{-\epsilon_i \delta\tau}|\phi_i\rangle$$

Maps to a branching importance sampled Monte Carlo

Enforce a fermionic solution via the "**fixed-node approximation**". Require nodes of projected wavefunction to be the same as trial. Variational error in energy. **Most significant approximation in DMC.**

Leads to a robust method with good properties: variational, consistently yields high-fraction of correlation energy, formally N^2-N^4 scaling, readily parallelized...

Cartoon Example

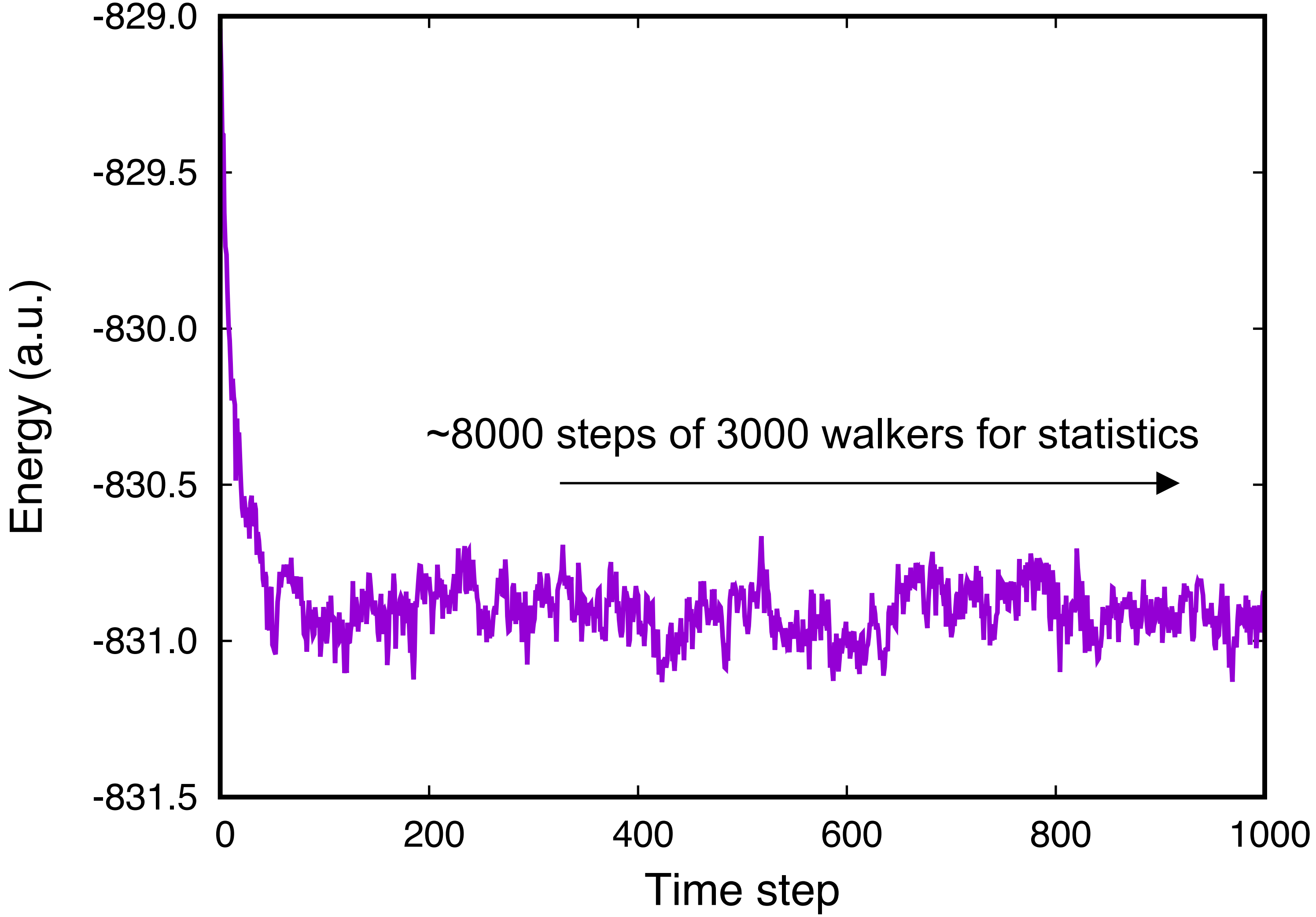


After initial projection to ground state, branching random walk has greatest density where wavefunction probability largest

Real World DMC: Bulk VO_2

Production run from Kylanpaa PRM **1** 065408 (2017).

200 electrons, 0.01 a.u. timesteps



Key features of DMC

Advantages	Disadvantages	Errors, Approximations
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.	Finite size scaling & cost in solid-state (Supercells). Small timestep needed for high Z. Unlike VMC, no explicit wavefunction obtained. Mixed estimator problem for non-commuting observables.	Potentially all controllable “Fixed node” Variational error in energy is key approximation.

Auxiliary Field QMC

AFQMC is projection method like DMC but works in orbital space. Same or similar as AFQMC used for "model" Hamiltonians.

Far fewer published AFQMC than DMC results. First production open source implementation is in QMCPACK.

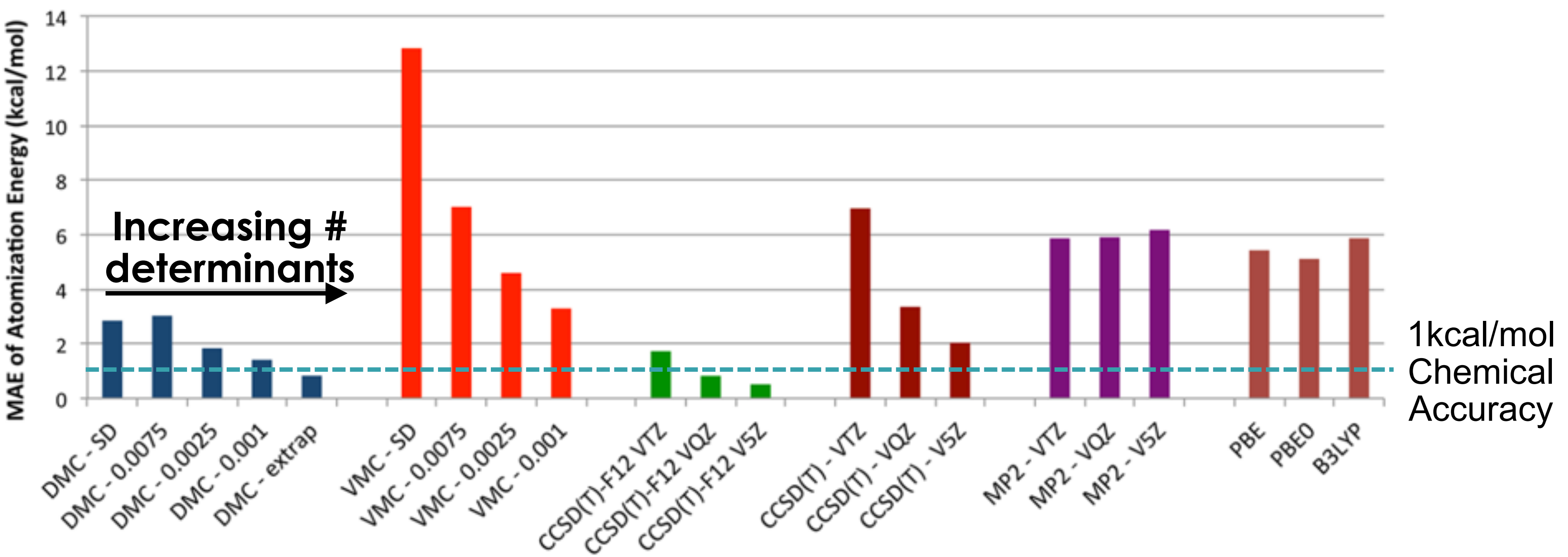
AFQMC	DMC
Strong basis set error	Works at basis set limit
Flexible treatment of core electrons	**Additional approximations needed for non-local potentials**
Spin-orbit, operators are easy	**Spin-orbit is not straightforward**
Direct connection to models	Trivial explicit correlation
K-point symmetries **(NEW)**	Memory friendly
Well suited to GPUs	**Complex workflow**
Simple workflow	
Overall costs (time, memory)	

See https://github.com/QMCPACK/qmcpack_workshop_2019 + YouTube

Molecular systems

Chemical accuracy <1kcal/mol achieved via the "linear method" for wf optimization of Umrigar et al. PRL (2007).

Trial wavefunctions use large multideterminant expansions DMC better than VMC.



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

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

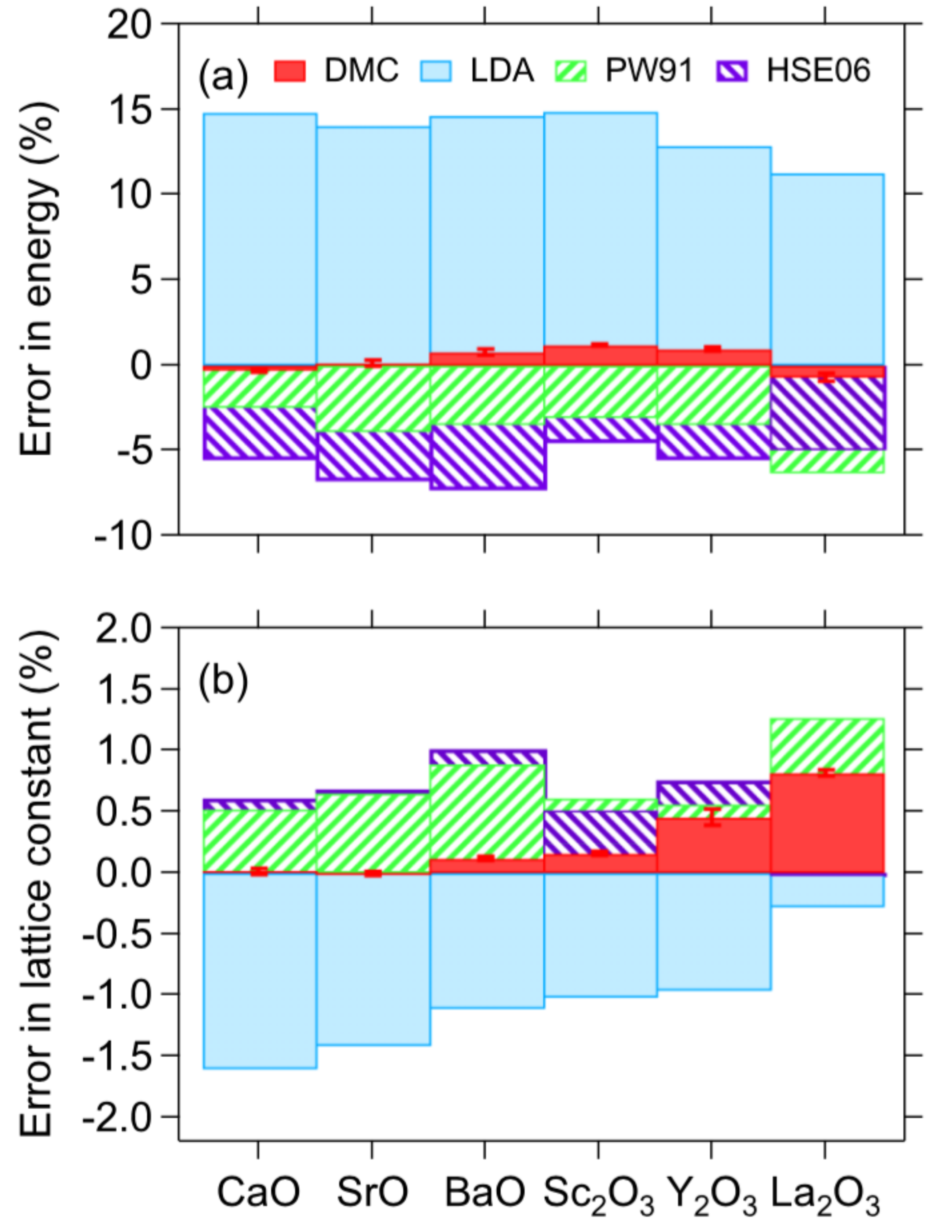
Solids: Metal oxides

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

Error increases for heavier elements.

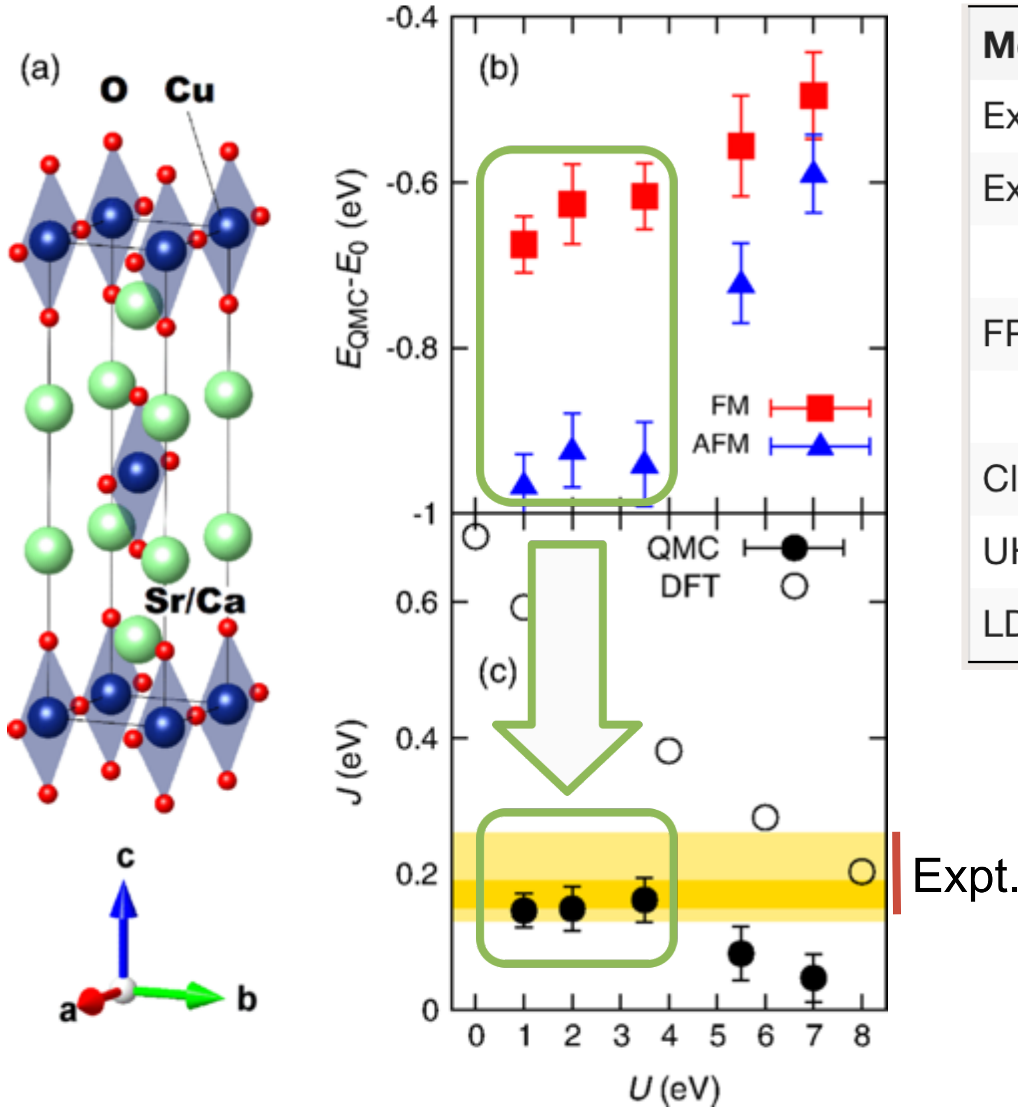
Recall: These are **not** exact calculations. Relative size of nodal and pseudopotential errors is not known.

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)

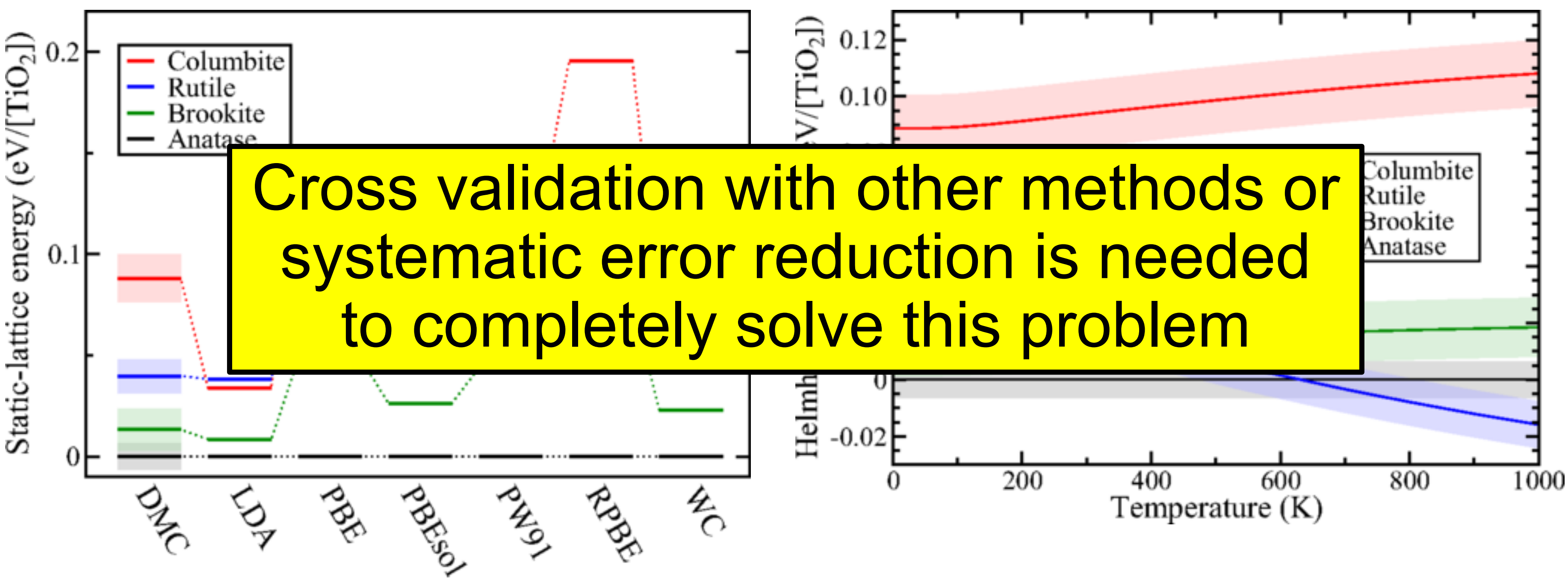
Other studies inc. La_2CuO_4:
L. Wagner et al. PRB **90** 125129 (2014), PRB **92** 161116 (2015)

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).



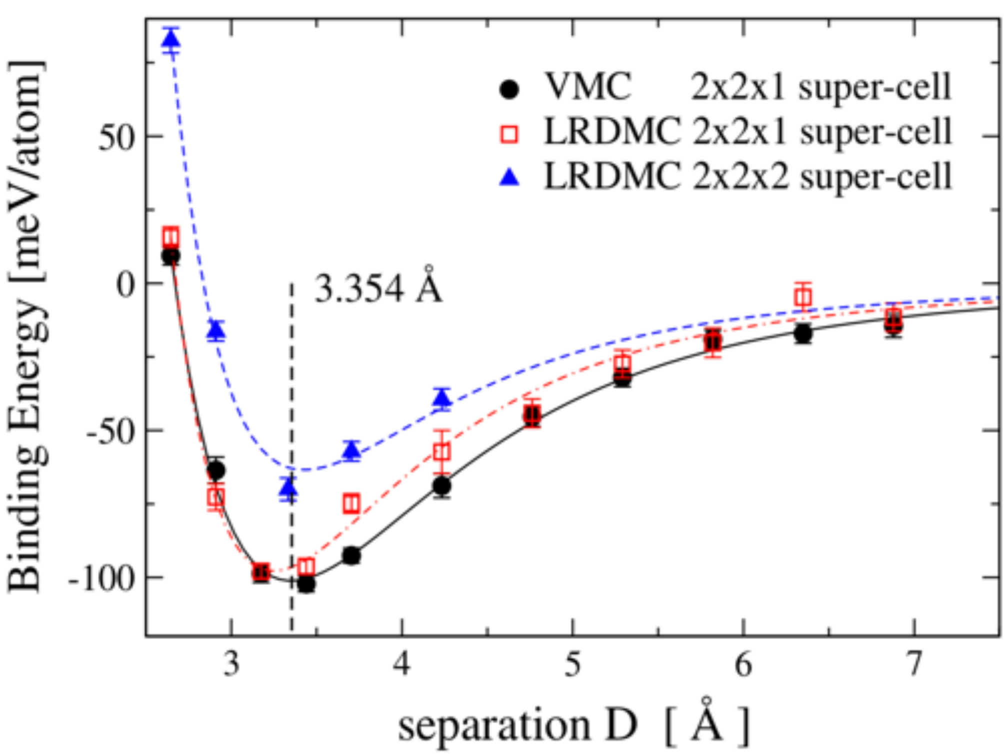
Cross validation with other methods or systematic error reduction is needed to completely solve this problem

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

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 & heterostructures.



DMC calculations with up to 64 atoms, 256 electrons.

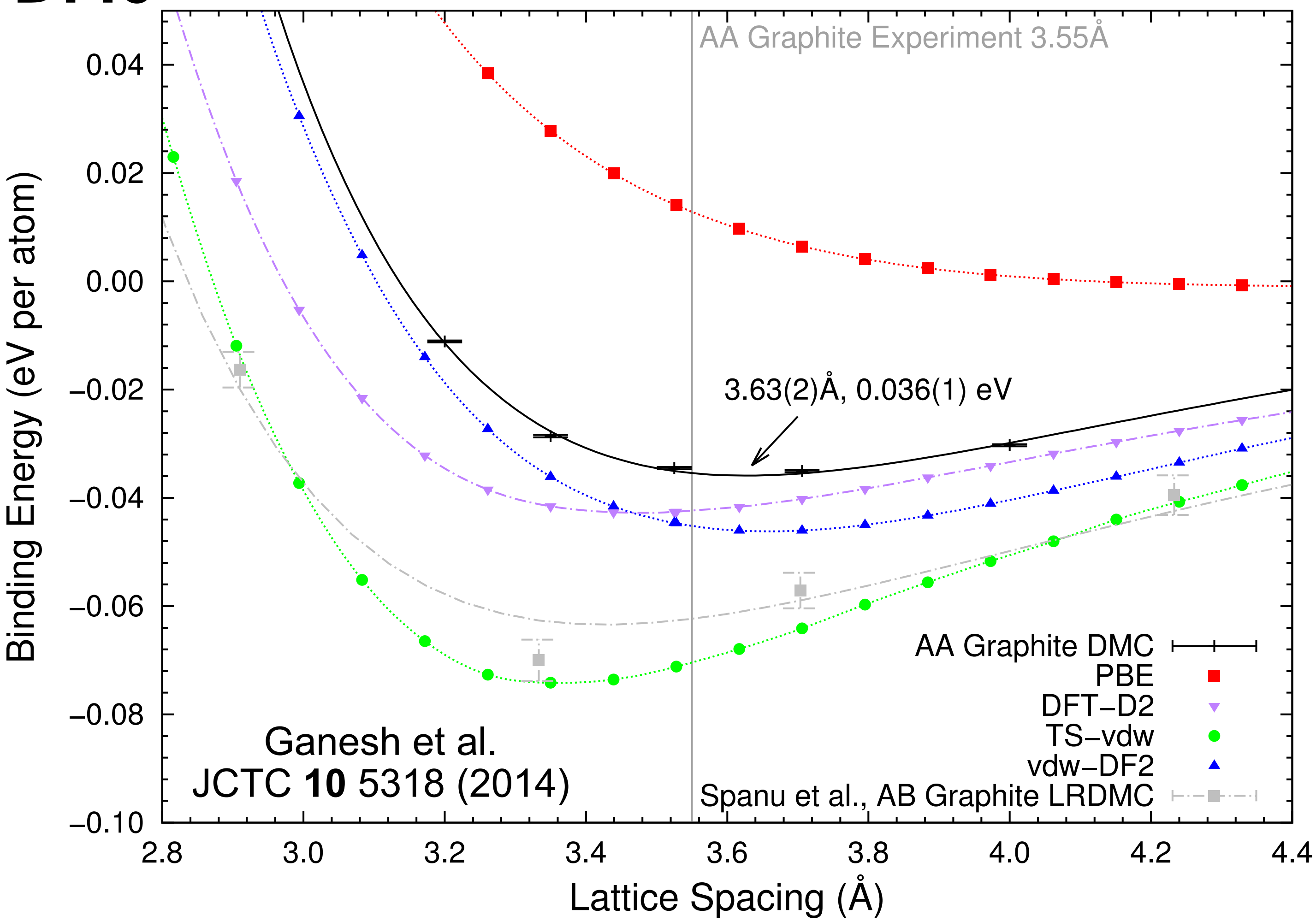
Simple, single determinant trial wavefunctions from DFT.

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 0.1A 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.

The Future

"The future is already here – it's just not very evenly distributed"

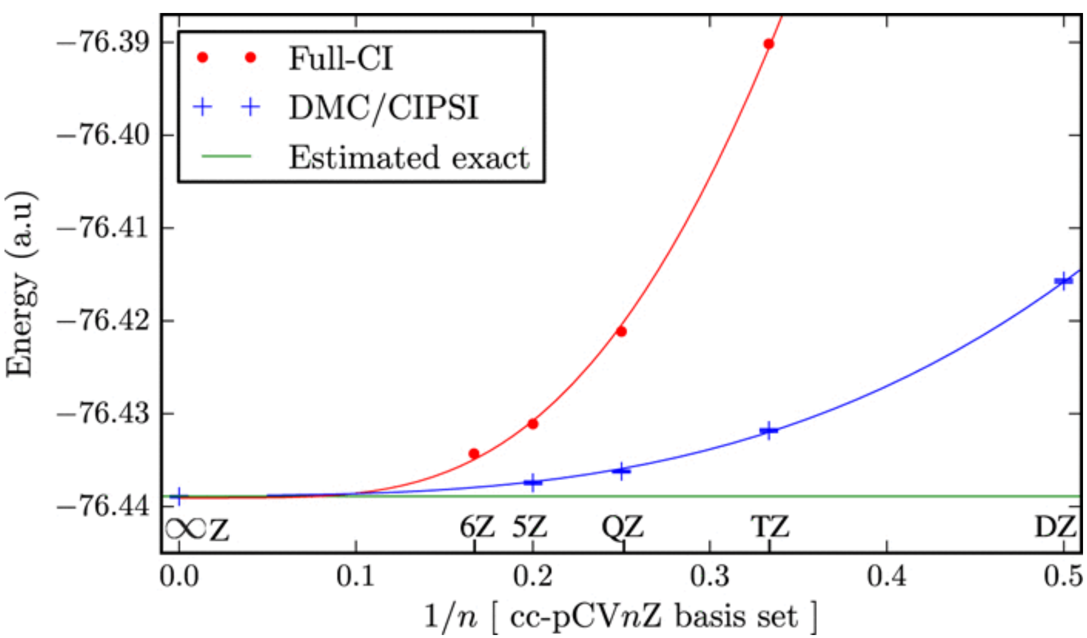
William Gibson

~~Towards~~ Systematic convergence

We can use selected-CI methods to build large multideterminant wavefunctions & reoptimize.

Pioneered for QMC by Toulouse group: Use CIPSI to perturbatively grow a wavefunction with a single threshold parameter.

Near push-button workflow developed for molecules.



H_2O molecule
−76.438 94(12) a.u. CIPSI-DMC
vs −76.438 9 a.u. Experiment

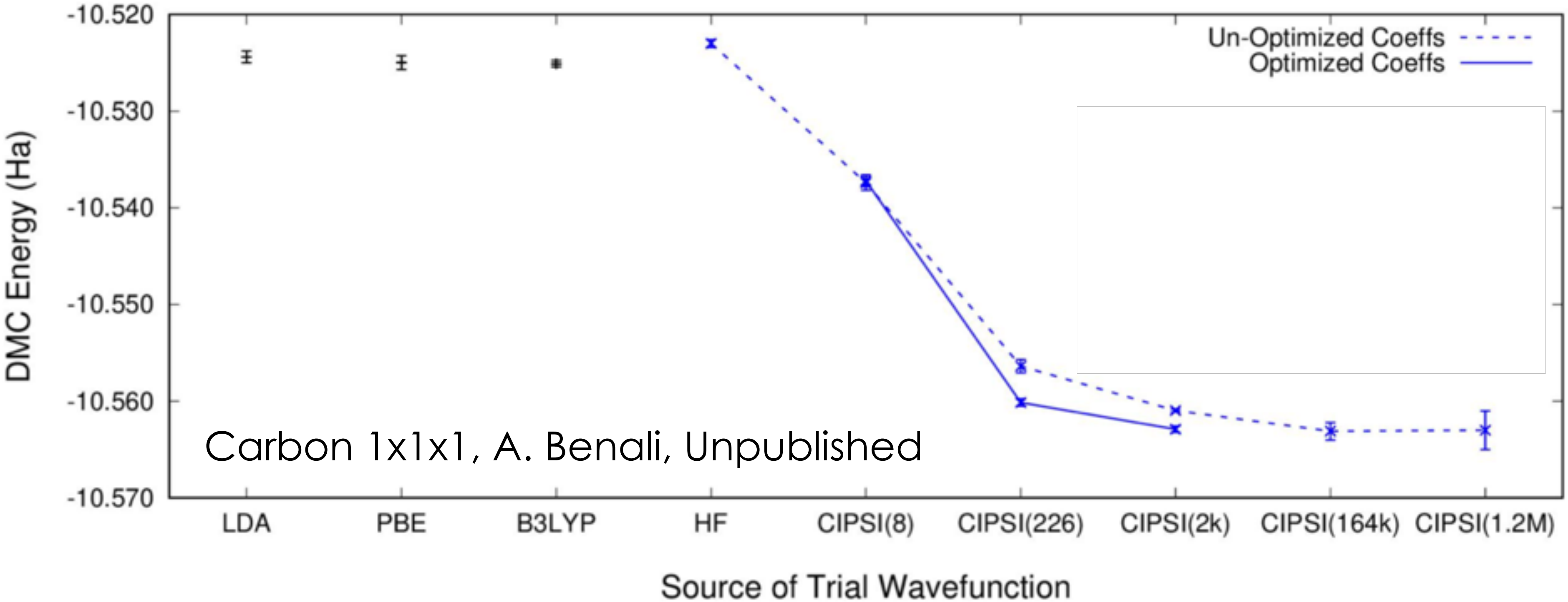
Most accurate theory calculation to-date

Caffarel et al. JCP **144** 151103 (2016)

Systematic convergence in solids

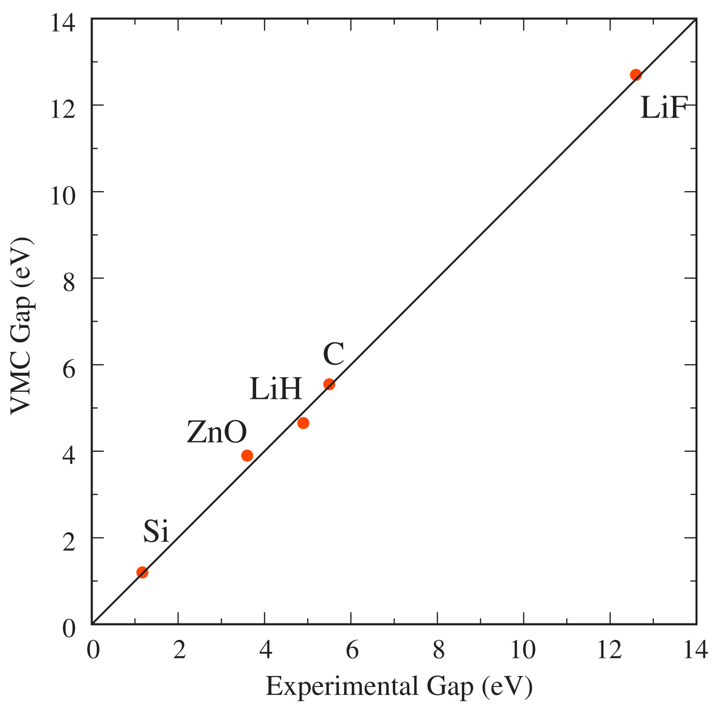
Similar techniques should work in solids – the question is how complex a solid can be treated?

Current practical bottleneck is LCAO interface, Gaussians



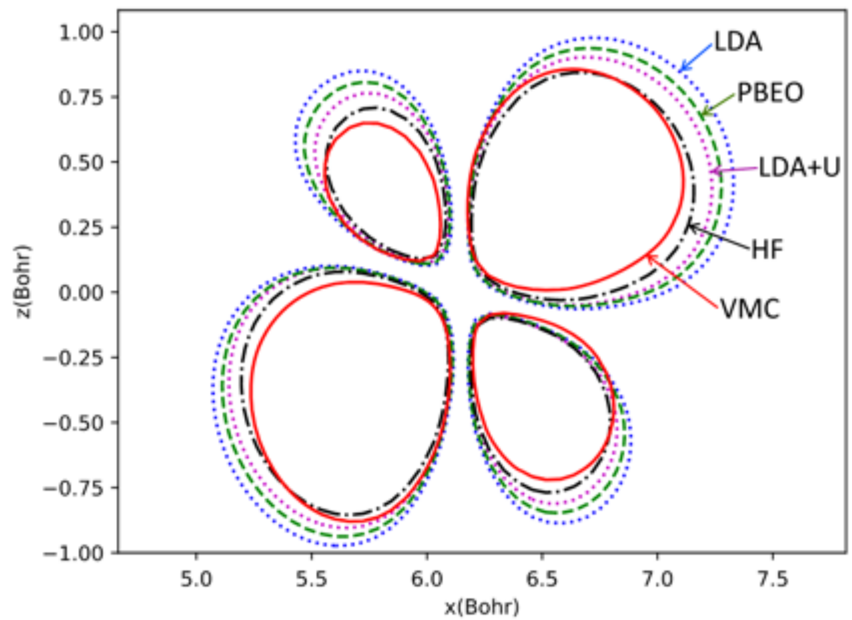
Convergent Excited states

Build multideterminant wavefunctions, selectively target and optimize for ground & excited states, match error (variance) between states.



Simple VMC gives accurate results!
No supercomputers used!

ZnO hole density isocontours

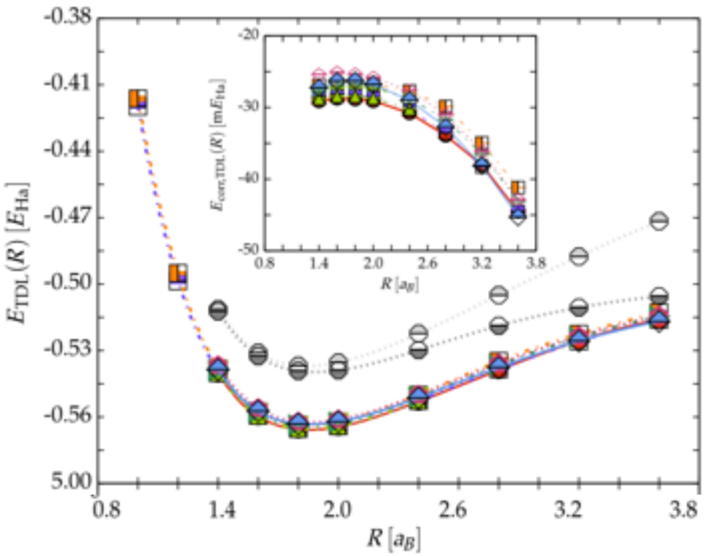


Analyze wavefunction to understand + guide G_0W_0 accuracy in ZnO

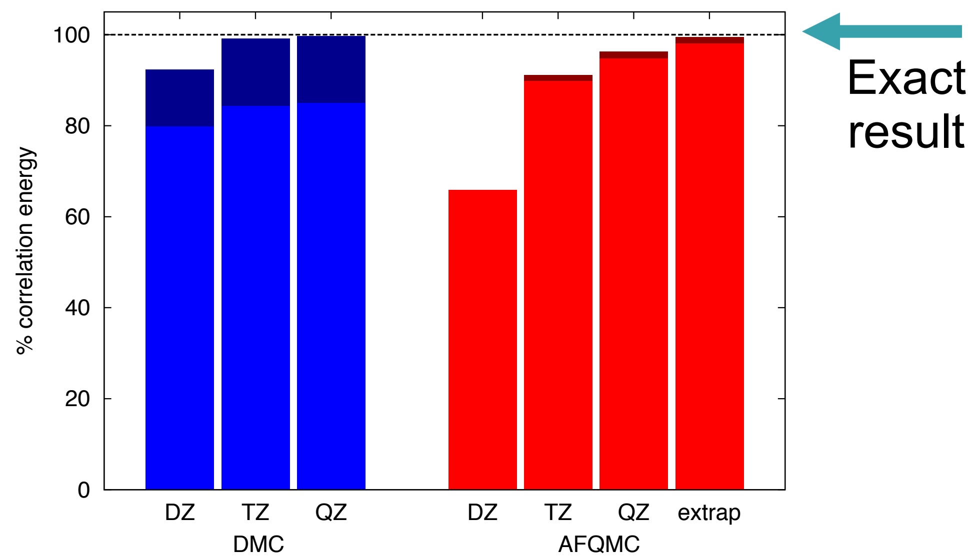
Zhao & Neuscamman PRL **123** 036402 (2019)

Cross-validation

Use of multiple, distinct methods will give stronger predictions and help drive methods improvement for strongly correlated 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.

Improving DFT functionals

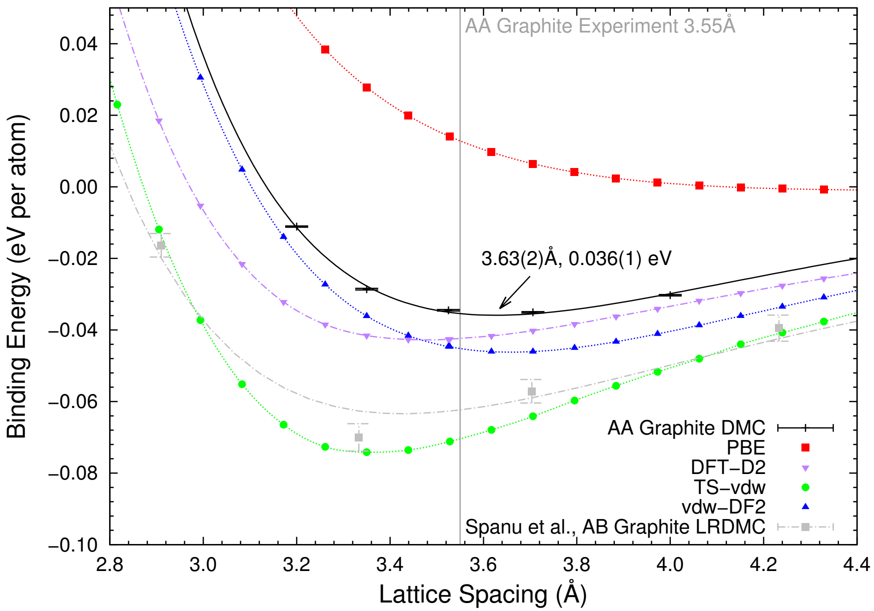
Clearly, this is a hard problem…

Use QMC data from real materials, models to:

- Choose best functional for given application
- Obtain improved understanding by analyzing many-body wavefunctions for solid-state

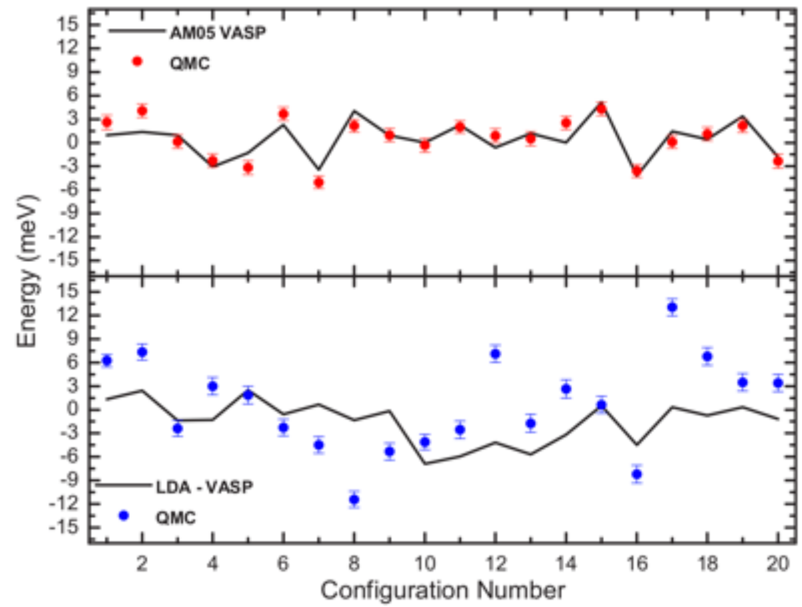
QMC can already inform DFT choice

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.

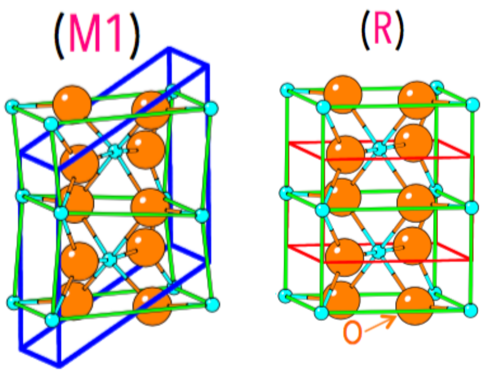


Mattsson et al.
PRB **90** 184105 (2014)

VO_2 metal-insulator transition and phase diagram

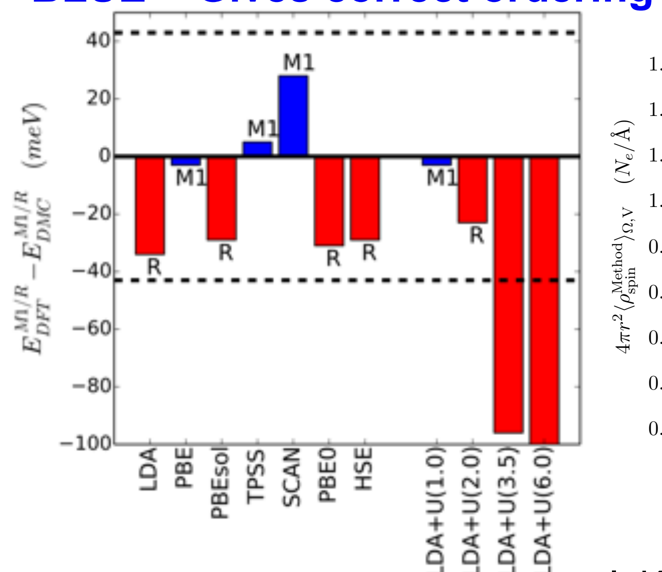
Long a challenge for ”band theories” to obtain the correct phase ordering and physics. M1 transitions to rutile phase at ~340K, becoming metallic. Analysis of the QMC charge density -- with good statistics -- finds that functionals have difficulty with the vanadium d electrons (presumably self-interaction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

Structure

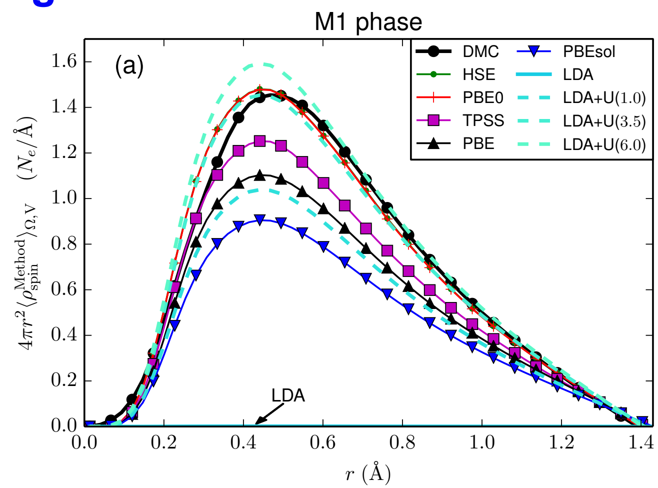


Phase stability

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 (dangerous) or help design one (preferred).

Analyzing the wavefunction

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

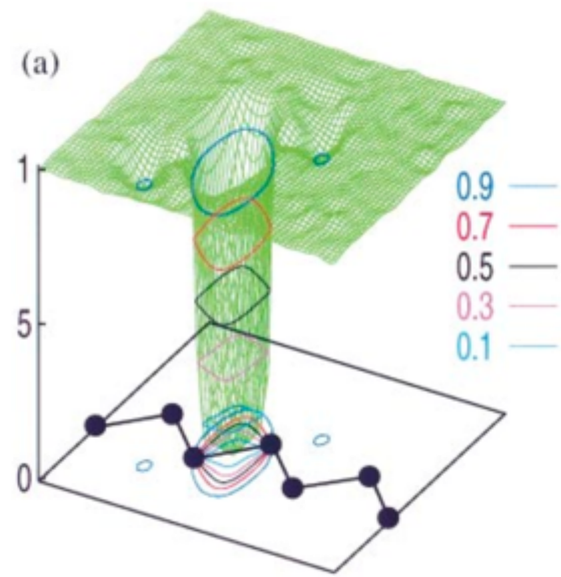
Accessible many-body quantities: density n(**r**), pair correlation function g(**r**,**r'**), density matrix n(**r**,**r'**), exchange correlation energy density e_{XC}(**r**),…

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

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

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

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



g(**r**,**r'**) spin parallel, one electron on bond center, Si (110) plane

Bulk silicon analysis

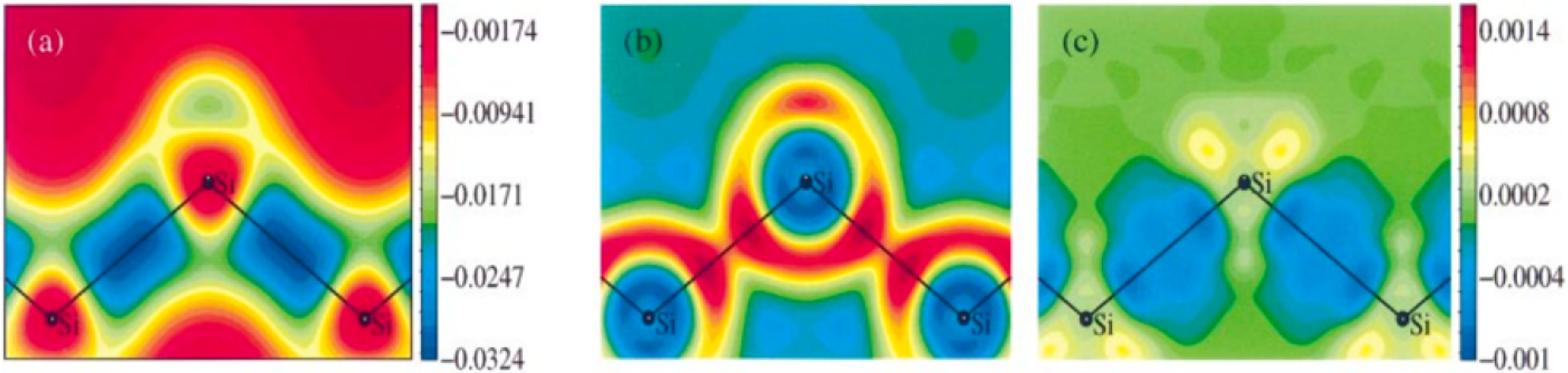


FIG. 4(color). Contour plots along the (110) plane for (a) $e_{xc}^{VMC}(\mathbf{r})$, (b) $e_{xc}^{VMC}(\mathbf{r}) - e_{xc}^{LDA}(\mathbf{r})$, and (c) $e_{xc}^{VMC}(\mathbf{r}) - e_{xc}^{ADA}(\mathbf{r})$. (b) and (c) have the same legend shown to the right of (c). The atoms and bonds are schematically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

Some evidence of real space cancelation of errors in LDA
ADA (averaged density approximation) performs better than LDA in this case.
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 with modern functionals.

Summary: Informing DFT

- QMC can be used to help select the most accurate existing functional today. Can connect to DMFT the same way. Similar to use of quantum chemistry for molecular systems.
- Analysis of many-body wavefunctions may yield greater understanding.
- Important to heed the lessons of Medvedev et al. Science (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, GW, DMFT and other theories.

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QMCPACK

www.qmcpack.org

Fully open source, github.com/QMCPACK. 50 contributors!

A New Generation of Effective Core Potentials Pseudopotentiallibrary.org

New many-body construction method H-Kr, L. Mitas and co-workers, JCP 2017, JCP 2018x2, arxiv 2019

Improved accuracy compared to previous potentials including for stretched+compressed bonds.

Open website, various quantum chemistry formats + UPF with KB projectors for plane wave codes