Ab initio Quantum Monte Carlo

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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.
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

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 Schrödinger 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$_3$C$_2$), the largest family of 2D nanomaterials. Robust predictions needed to guide synthesis.

New phenomena

Neutrons show $\alpha$-RuCl$_3$ “is close” to Kitaev quantum spin liquid. Models for QSL depend strongly on Hamiltonian parameters.
DFT challenges...

Word cloud of “popular” DFTs

Many DFT approximations to choose from


+ comment & reply.

~ Energies & densities should be simultaneously improving.
Empirical fitting has reversed this trend.

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

Exact released-node DMC calculation
Exponential scaling
Parameterized in LDA-DFT by Perdew & Zunger (1982)

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 $\text{Y}_2\text{O}_3$:$\text{Mn}$ emission

Hybrid DFT is too low.

$O(1M)$ CPU hours

No heroics.
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

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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  – What is achieved today?
  – Why is the field growing?

• Quantum Monte Carlo Methods
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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 Schrödinger equation: Monte Carlo 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.

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

100x increase in cost to reduce error 10x! Sample accurately (importance sampling) Plan calculations carefully!
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
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

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

(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

Other options: Backflow, Geminals…

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

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

e.g. Drummond et al. PRB 70 235119 (2004)
## Key features of VMC

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Explicit form of trial wavefunction</td>
<td>Finite size scaling for periodic calculations</td>
</tr>
<tr>
<td>• Can use any trial wavefunction we can imagine</td>
<td>Explicit form of trial wavefunction</td>
</tr>
<tr>
<td>• Easy to compute any observable</td>
<td>• Limited to forms of trial wavefunction we can imagine - high accuracy difficult for solids, correlated physics.</td>
</tr>
<tr>
<td>• Simple Monte Carlo – no timestep error or other discretization introduced</td>
<td>• Potentially many parameters to optimize reliably. Not yet automated.</td>
</tr>
</tbody>
</table>
Diffusion Quantum Monte Carlo

Project out ground state to minimize trial wavefunction dependence.

Write the time dependent Schrodinger equation in *imaginary time*

$$\frac{\partial |\psi\rangle}{\partial \tau} = -\hat{H} |\psi\rangle$$

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

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

~8000 steps of 3000 walkers for statistics
# Key features of DMC

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Errors, Approximations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gives very accurate and robust results, even with simple nodal surfaces/trial wavefunctions.</td>
<td>Finite size scaling &amp; cost in solid-state (Supercells). Small timestep needed for high Z. Unlike VMC, no explicit wavefunction obtained. Mixed estimator problem for non-commuting observables.</td>
<td>Potentially all controllable “Fixed node” Variational error in energy is key approximation.</td>
</tr>
</tbody>
</table>
**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.

<table>
<thead>
<tr>
<th>AFQMC</th>
<th>DMC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Strong basis set error</strong></td>
<td>Works at basis set limit</td>
</tr>
<tr>
<td>Flexible treatment of core electrons</td>
<td>Additional approximations needed</td>
</tr>
<tr>
<td>Spin-orbit, operators are easy</td>
<td>for non-local potentials</td>
</tr>
<tr>
<td>Direct connection to models</td>
<td>Spin-orbit is not straightforward</td>
</tr>
<tr>
<td>K-point symmetries (NEW)</td>
<td>Trivial explicit correlation</td>
</tr>
<tr>
<td>Well suited to GPUs</td>
<td>Memory friendly</td>
</tr>
<tr>
<td>Simple workflow</td>
<td>Complex workflow</td>
</tr>
<tr>
<td><strong>Overall costs (time, memory)</strong></td>
<td></td>
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See [https://github.com/QMCPACK/qmcpack_workshop_2019](https://github.com/QMCPACK/qmcpack_workshop_2019) + YouTube
Molecular systems

Chemical accuracy <1 kcal/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)
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.

Copper oxides

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

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

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

Expt. Other studies inc. La$_2$CuO$_4$:
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 0.1 Å 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$_2$O molecule
$-76.43894(12)$ a.u. CIPSI-DMC vs $-76.4389$ 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

Carbon 1x1x1, A. Benali, Unpublished
**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!

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

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

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

Spanu et al., AB Graphite LRDMC

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

Spin-density analysis

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.

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) $e_{xc}^{VMC}(r)$, (b) $e_{xc}^{VMC}(r) - e_{xc}^{LDA}(r)$, and (c) $e_{xc}^{VMC}(r) - e_{xc}^{ADA}(r)$. (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)

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.

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