

# Choosing a **QMC** Project

## *Guidelines and Examples*

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# Outline

Paul's 12 points to consider when picking a QMC project

Examples of recent projects, my view of risks & strengths

# Notes and disclaimers

Many of the considerations are common to other computational sciences

I am only listing 12 points (there are more)

These are opinions intended for consideration and discussion, but are not necessarily facts or “rules”

A breakthrough might ignore most of these!

# #1: Consider your audience

Structure your investigation so that the greatest audience will be interested. Make your results relevant to others.

Obtaining one more digit in accuracy is usually less interesting than addressing a long established controversy, or identifying a new one.

Will experimentalists be interested?

Will the wider electronic structure community be interested?

Can you “prove” or disprove a mechanism?

E.g. Show that an interaction is too large/small to be responsible for an important property of a class of materials.

## **#2: Just because you have a hammer, it does not mean everything is a nail**

Carefully consider whether QMC is a good choice:

Predictive accuracy can be determined by many factors and you must balance the overall error.

e.g. If the problem has disorder/many possible defect configurations/large number of isomers, you will not see the full picture unless all can be addressed at QMC level.

Other methods may be able to compute more properties and develop a better overall picture.

Relativistic effects (spin orbit only just being developed in QMC).

Temperature effects.

### **#3: Favor studies of systems where other methods have substantial difficulty over small improvements in accuracy**

Systems with d-states or where van der Waals interactions are important.

Where different oxidation states are present in same/different materials.

Where the DFT band gap is badly wrong.

Where the wavefunction will have multireference character.

...

## **#4: Favor well-controlled and easily reproduced studies to determine qualitative mechanisms over studies treating full materials/chemical complexity**

Leads to more robust and less ambiguous results.

Simplify geometry (relaxed vs unrelaxed).

Study generic features of parent compounds, chemicals.

Corollary: Good to eventually reach full complexity and full accuracy.

## **#5: Consider how you can leverage cheaper methods to minimize the number of QMC calculations required**

Use QMC to validate a particular choice of cheaper electronic structure method, or build a correction scheme when you understand the failings.

A correction scheme can be used by others.

## **#6: Test pseudopotentials early**

YOU might be the first person to run an element in QMC!

Particularly for novel elements, check simple properties early in the investigation. E.g. dimer properties

If you change the pseudopotential you will have to recompute everything.

## **#7: Build in an early check of your calculations**

From early runs, estimate the required statistics and overall cost. If the calculations do not look to be affordable, replan or postpone a few years.

Perform a full finite-size scaling analysis with VMC before the more costly DMC.

Perform full analysis on one molecule before starting calculations on a large set of molecules.

## **#8: A study does not have to be expensive to be worthwhile**

Lots of interesting physics and chemistry in small systems.

Most QMC studies will be new and will be publishable.

Also, just because a study is expensive does not mean it is correct!

## **#9: Consider the likely degree of error cancelation when assessing difficulty**

Error cancelation is most favored when comparing similar systems

e.g. For binding between two graphene planes, pseudopotential errors are likely to mostly cancel since only carbon is involved.

Highlights the importance of well-controlled benchmark studies considering many different species, chemical bonds, and types of solid.

## **#10: Consider the finite size error when assessing difficulty**

Can not be any better than DFT or quantum chemistry for the same system.

Make sure the geometry/cell size is converged to better than that needed by the cheaper & more approximate electronic structure method.

# **#11: Consider the statistical properties of the properties of interest**

Bulk studies are usually much easier statistically than defect studies

Cohesive energies are reported per primitive cell (intensive property), so as larger supercells are run, improved statistics are obtained. Not the case for a defect such as a vacancy.

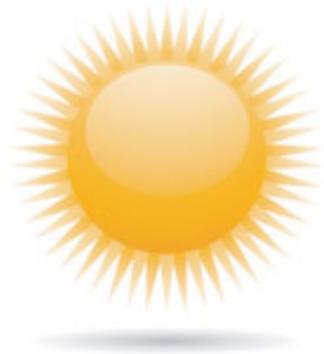
## #12: Consider many-body properties

Although only briefly touched-upon at this training, QMC is a many-body method with the full wavefunction potentially available.

e.g. density matrix, correlation functions, entanglement...

# Examples

# Ratings



Sunny outlook



A few worries

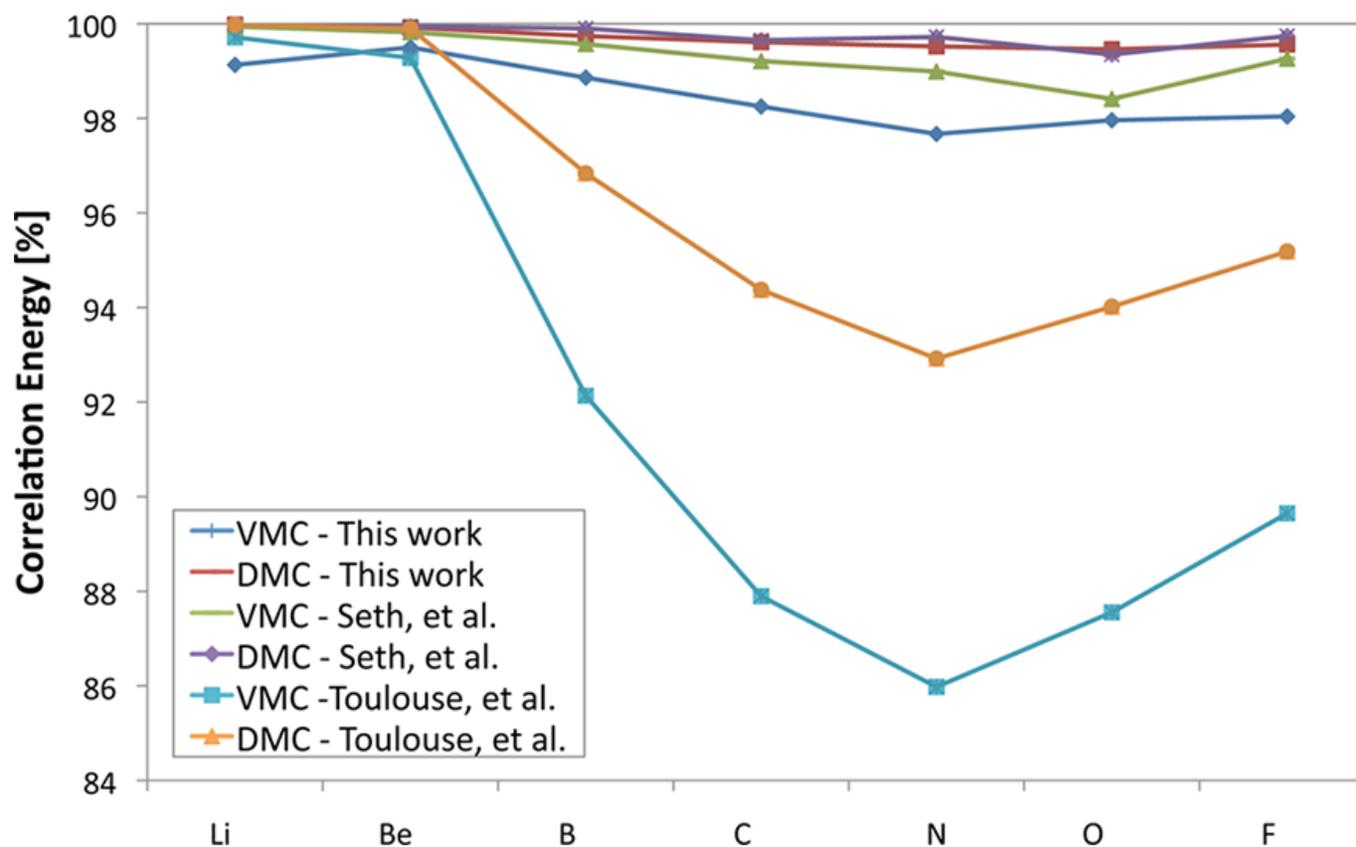


Large risks

# Benchmarking the accuracy of QMC for molecules

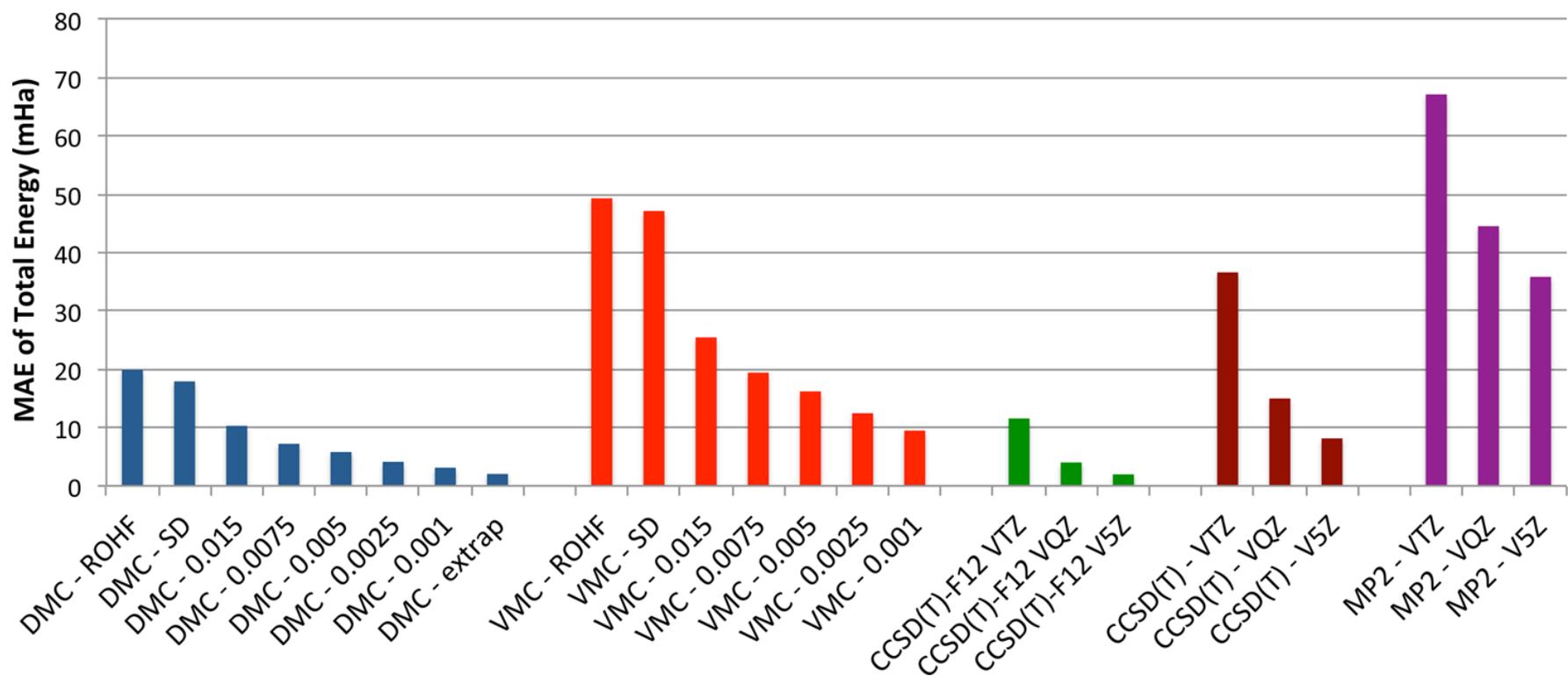
“Multideterminant Wave Functions in Quantum Monte Carlo”, M. A. Morales, ..., G.E.Scuseria. JCTC **8** 2182 (2012) <http://dx.doi.org/10.1021/ct3003404>

High accuracy achievable for atoms:



# Benchmarking the accuracy of QMC for molecules

Testing accuracy for G1 test set ( $C_2H_2$ , CN,  $H_2O$ , NaCl,  $SiH_4$ , SiO...), going beyond single determinant “standard recipe”. MAE of 0.8kcal/mol achieved for atomization energies, i.e. Chemical accuracy.

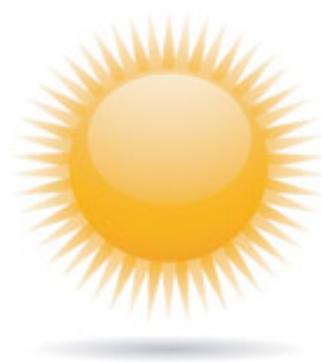


See also Nemeč et al. JCP **132** 034111(2010)

<http://dx.doi.org/10.1063/1.3288054> all electron single determinant tests for same test set (CASINO code).

# Benchmarking the accuracy of QMC for molecules

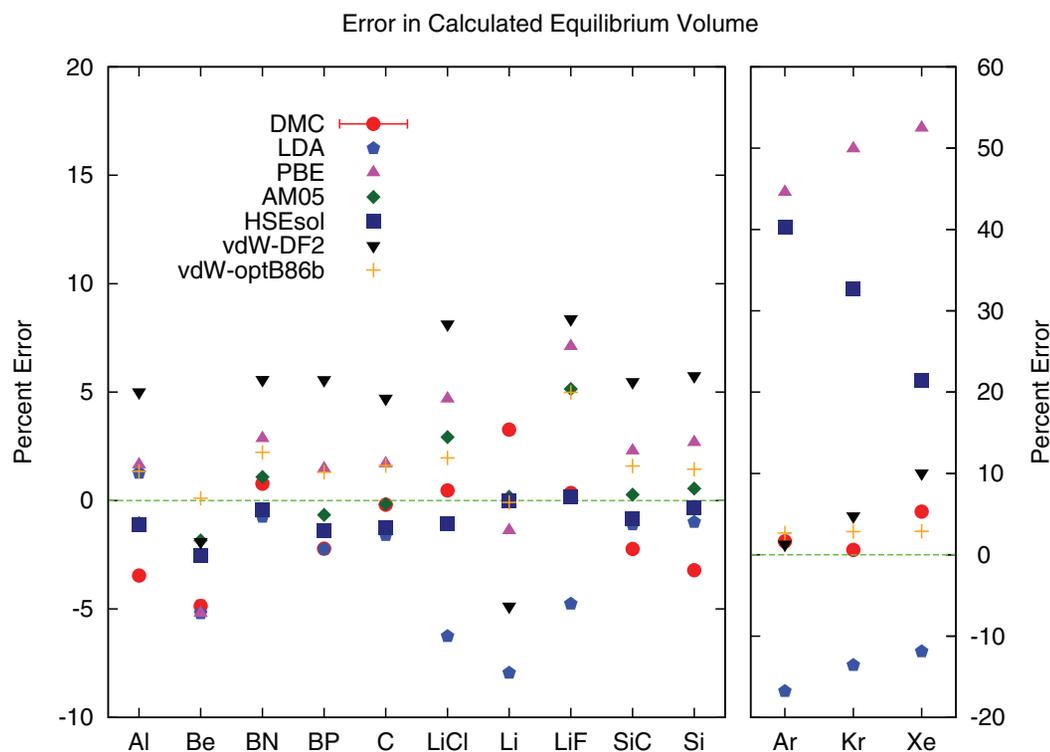
- + Audience: wider electronic structure and quantum chemistry community
- + You can stop after one molecule if you find problems
- + Individual molecular calculations can be cheap
- + Important to show achievable accuracy of method
- We already have methods that can solve the G1 set accurately (and quickly)



# Benchmarking the accuracy of QMC for solids

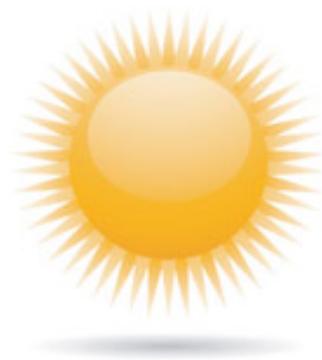
Analysis of structural properties ( $V$ ,  $B_0$ ) of ionic, metallic, covalent and van der Waals solids using “standard recipe” single determinant Slater-Jastrow pseudopotentials. Careful convergence of calculations. Finds high accuracy over whole set of solids.

“Quantum Monte Carlo applied to solids” L. Shulenburger & T. R. Mattsson PRB **88** 245117 (2013) <http://dx.doi.org/10.1103/PhysRevB.88.245117> Editors’ Suggestion.



# Benchmarking the accuracy of QMC for solids

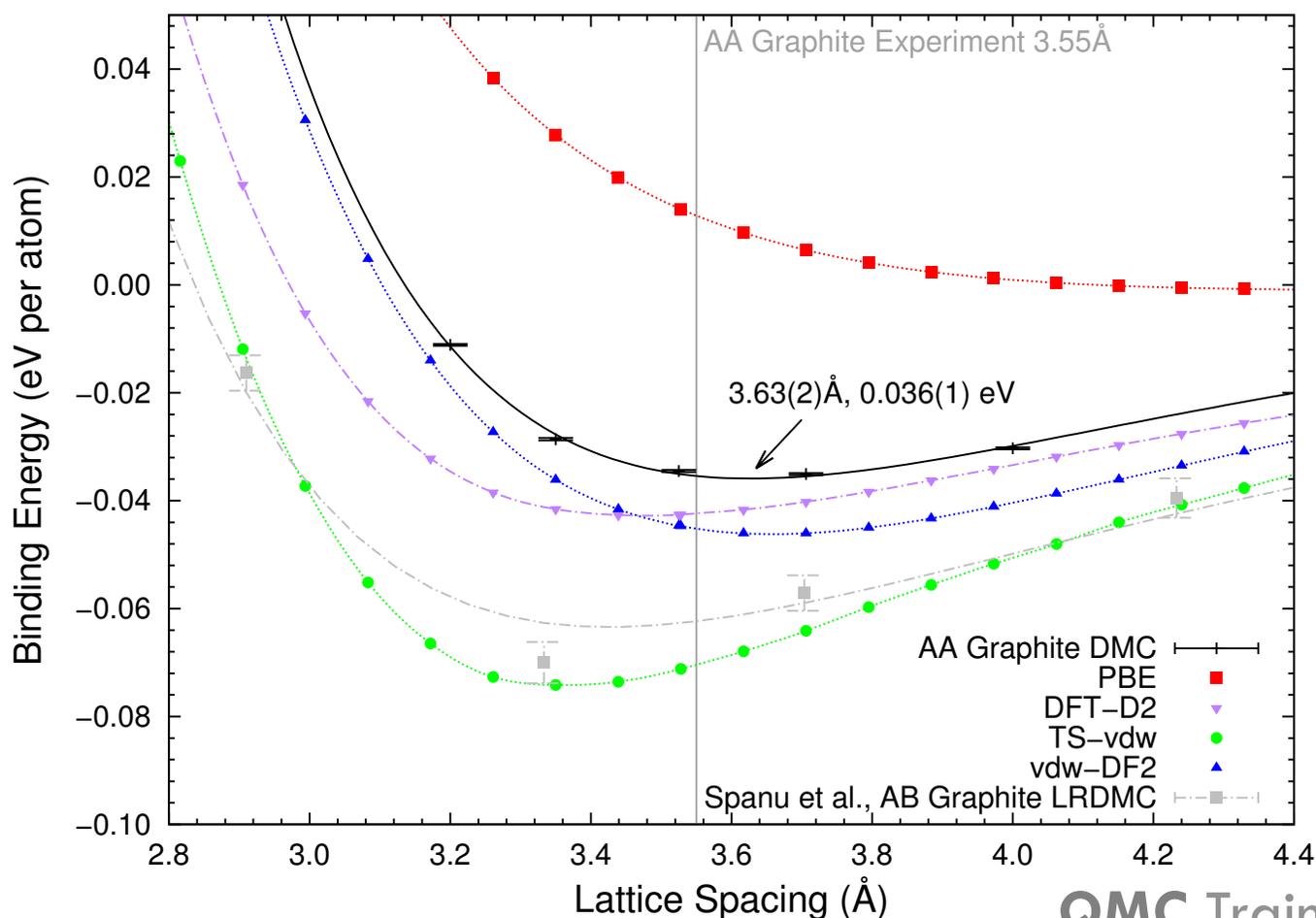
- + Audience: wider electronic structure and quantum chemistry community
- + You can stop after one solid if you find problems
- Solids are more expensive than molecules
- + Important to show achievable accuracy of method
- + We don't have other methods that deliver consistent accuracy for solids



# Binding and diffusion of lithium in graphite

DMC calculations accurately predict the lattice constant and binding energy of A-A graphite relative to A-B graphite. When dilute Li is added, self-consistent van der Waals DFTs outperform empirical schemes due to the importance of charge transfer.

P. Ganesh, J. Kim, C. Park, M. Yoon, F. A. Reboredo, and P. R. C. Kent (submitted).



# Binding and diffusion of lithium in graphite

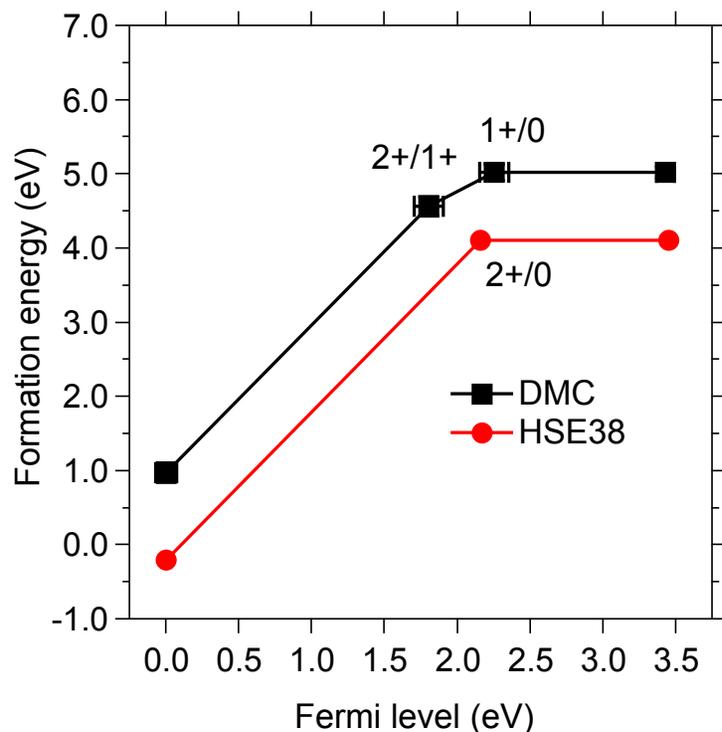
- + Audience: wider electronic structure and quantum chemistry community + smaller Li-ion battery modeling community
- + There is a well identified problem with the Li-graphite binding energy (voltage at low concentration)
- + A-B Graphite previously run by Spanu, Galli with good results
- + Previous good results for carbon diamond and carbon vacancy
- Comparative expense of lithium binding energy calculations compared to pure graphite binding (low millions vs hundreds of thousands of hours)



# The vacancy in ZnO

DMC calculations rule out the oxygen vacancy as the source of persistent n-type conductivity in ZnO. Confirms previous DFT predictions but finds (i) much higher oxygen vacancy formation energy that HSE or other DFT approximations, (ii) finds a positive U behavior in contrast to the DFT.

“Ab initio many-body calculations of the oxygen vacancy in ZnO”, J. A. Santana, J. T. Krogel, J. Kim, P. R. C. Kent, and F. A. Reboredo, <http://arxiv.org/abs/1406.3169>



# The vacancy in ZnO

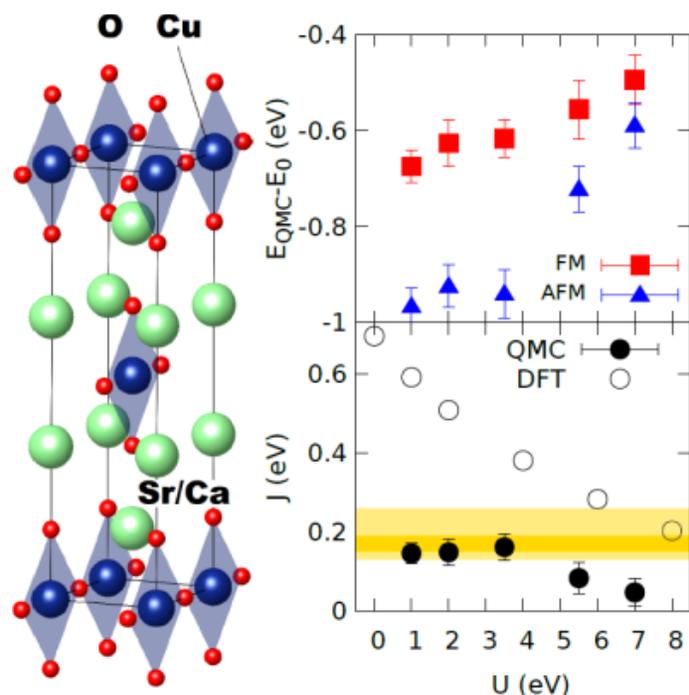
- + Audience: Well-recognized that persistent photoconductivity and role of vacancy is important. Experimental+theoretical communities.
- + Although band gap is poor in DFT, overall electronic structure is relatively well-predicted
- +/- Needed to carefully develop Zn potential
- Won't know quality of results are until large cells are run, but could stop at neutral vacancy if problems are found
- Possible finite size errors and memory limitations with large defect cells (in bulk, symmetry reduces usage)



# Computing the exchange coupling in cuprates

Within a variational scheme (a non-empirical scheme), DMC predicts exchange constants in good agreement with experiment for  $\text{Ca}_2\text{CuO}_3$ . Indicates promise for describing ground state properties of strongly correlated materials.

K. Foyevtsova, J. T. Krogel, J. Kim, P. R. C. Kent, E. Dagotto, F. A. Reboredo. PRX 4 031003 (2014) and <http://dx.doi.org/10.1103/PhysRevX.4.031003>



Also see QMC results for  $\text{La}_2\text{CuO}_4$ , with more properties considered including phonons, L. Wagner & P. Abbamonte <http://arxiv.org/abs/1402.4680>

# Computing the exchange coupling in cuprates

- + Audience: Well-recognized that the electronic structure of cuprates is important, but the experimentalists have already measured the exchange constants
- The underlying DFT ground state could be badly wrong (is wrong in pure LDA/PBE), giving rise to poor trial wavefunctions
- +/- Need to optimize trial wavefunctions via DFT+U, hybrid, or a new method
- +/- Needed to carefully develop Cu potential
- + Larger cells sample more spins, giving improved statistics
- Won't know quality of results until large cells are run



# Summary

It is important to consider overall complexities, costs and “risks” of a QMC investigation. They are different from established/conventional electronic structure methods.

Small molecules and bulk properties are attractive for initial QMC projects.

**Questions?**