SAND2019-5983C

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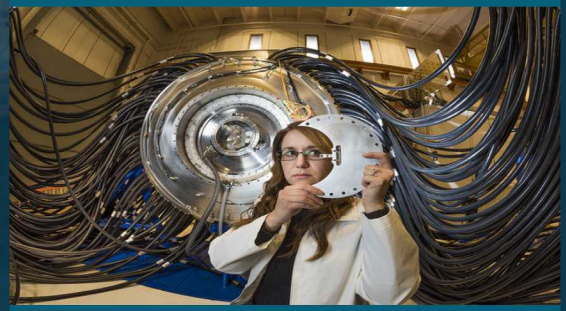
Progress from the Methods Development Effort of the Center for the Predictive Simulation of Functional Materials



PRESENTED BY

Luke Shulenburger

U.S. DEPARTMENT OF ENERGY | NNSA

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Center for the Predictive Simulation of Functional Materials

DOE Computational Materials Science Center

PI: Paul Kent

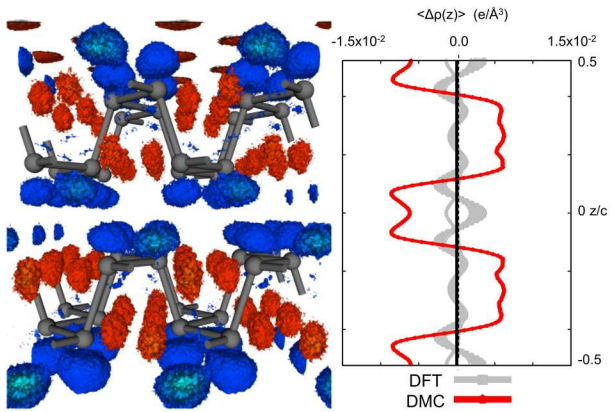
Goal: *The development, application, validation, and dissemination of parameter-free methods and open source codes to predict and explain the properties of functional materials for energy applications*.

Berkeley UNIVERSITY OF CALIFORNIA · Lawrence Livermore National Laboratory · Sandia National Laboratories · Argonne NATIONAL LABORATORY · NC STATE UNIVERSITY · OAK RIDGE National Laboratory

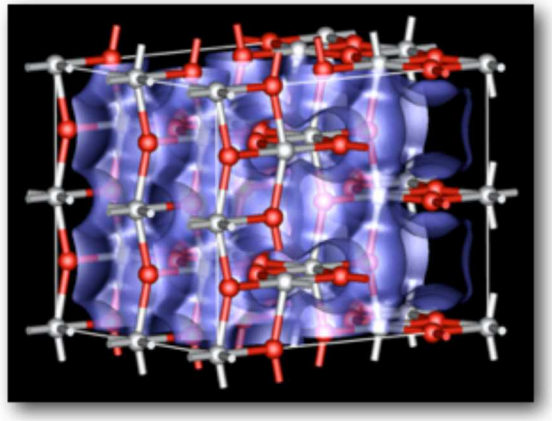
The Focus: Quantum Monte Carlo

These statistical methods, both real space and orbital space, solve the Schrodinger equation directly, with only a few, well defined and potentially systematically reducible errors. The methods are becoming able to cross-validate themselves.

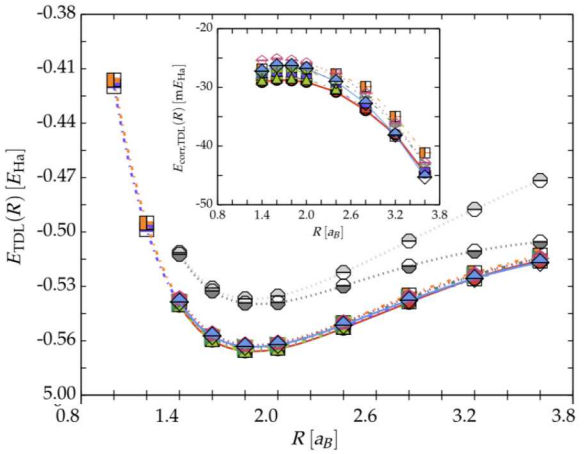
Our initial materials: Mainly binary oxides – NiO, FeO, VO_2...



Binding of few layer phosphorus
Shulenburger NanoLett. 2015



TiO_2 stability
Luo NJP 2016,
Trail PRB 2017



H_{10} chain, many methods
Motta PRX 2017
(Simons Collaboration)

Why are the approximations?

Monte Carlo Samples a probability distribution

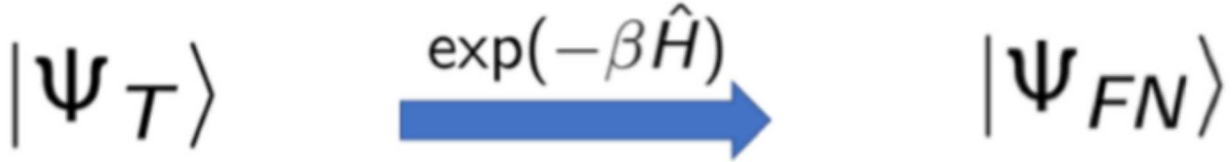
- Electrons are Fermions! (wavefunction is not >0 everywhere)

Use guiding (trial) wavefunction, Ψ, for importance sampling and for fixed node approximation

Ψ is not the exact many-body wavefunction

- Generally built using single particle orbitals calculated externally
- Energy only depends on Ψ=0 manifold
- Global imperfections bias other observables

A bird's eye view



A bird's eye view

$|\Psi_T\rangle$ $\xrightarrow{\exp(-\beta\hat{H})}$ $|\Psi_{FN}\rangle$

$\xrightarrow{\exp(-\beta\hat{H})}$

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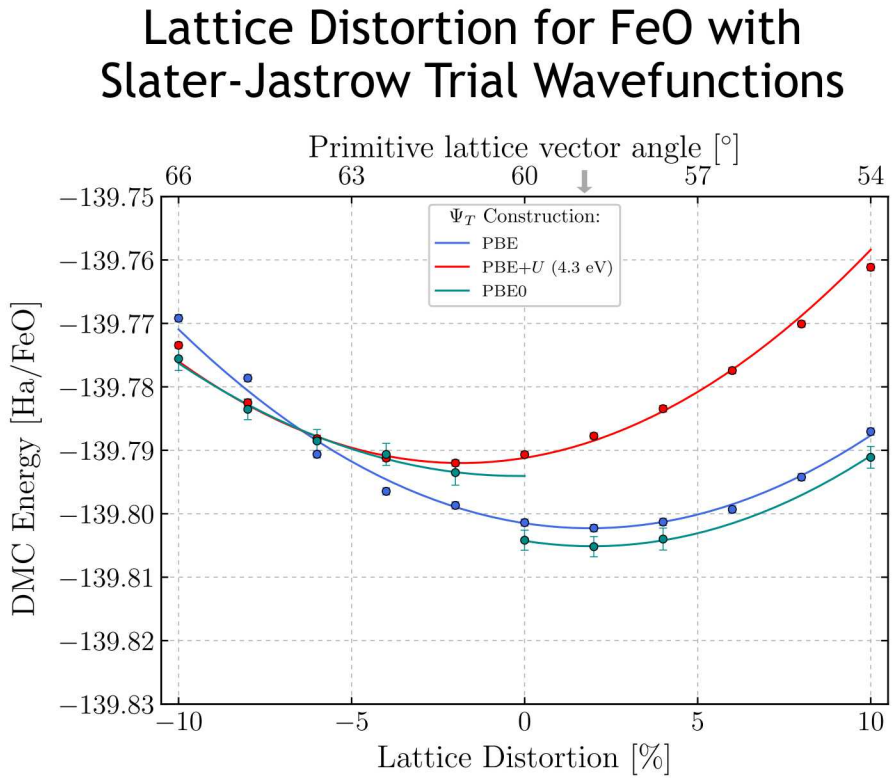
Checking in with a classic - FeO

Classic example of strong correlation (Mott Insulator)

Focus on impact of trial wavefunction construction

- Little sensitivity in weakly correlated materials like SiO_2
- Equilibrium Geometry, Gap, Moments

Choice of single particle orbitals had a strong and uncontrolled effect



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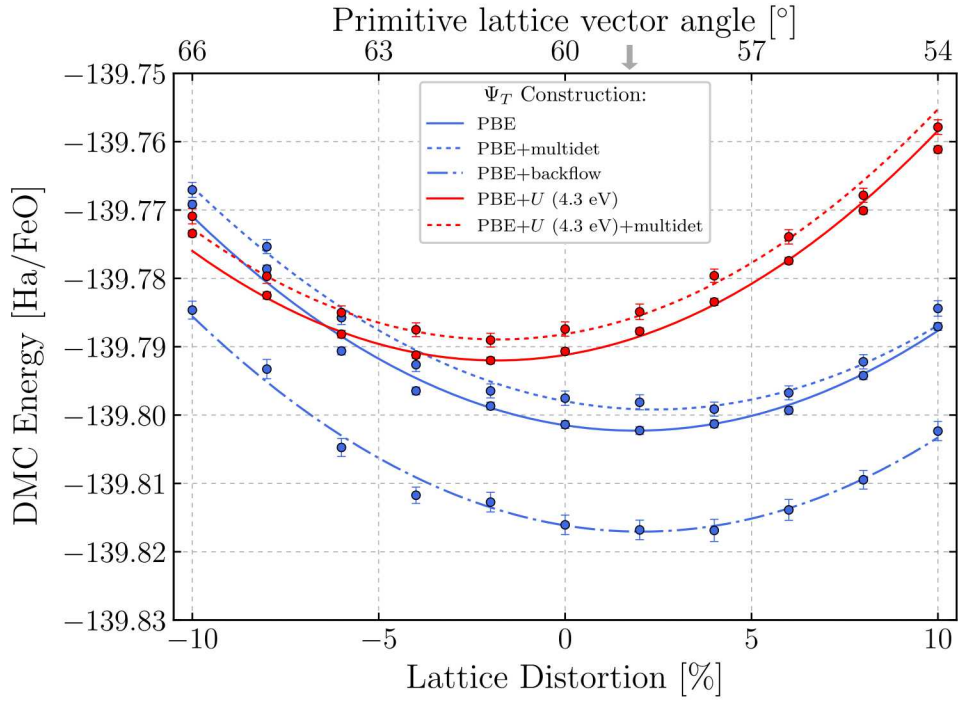
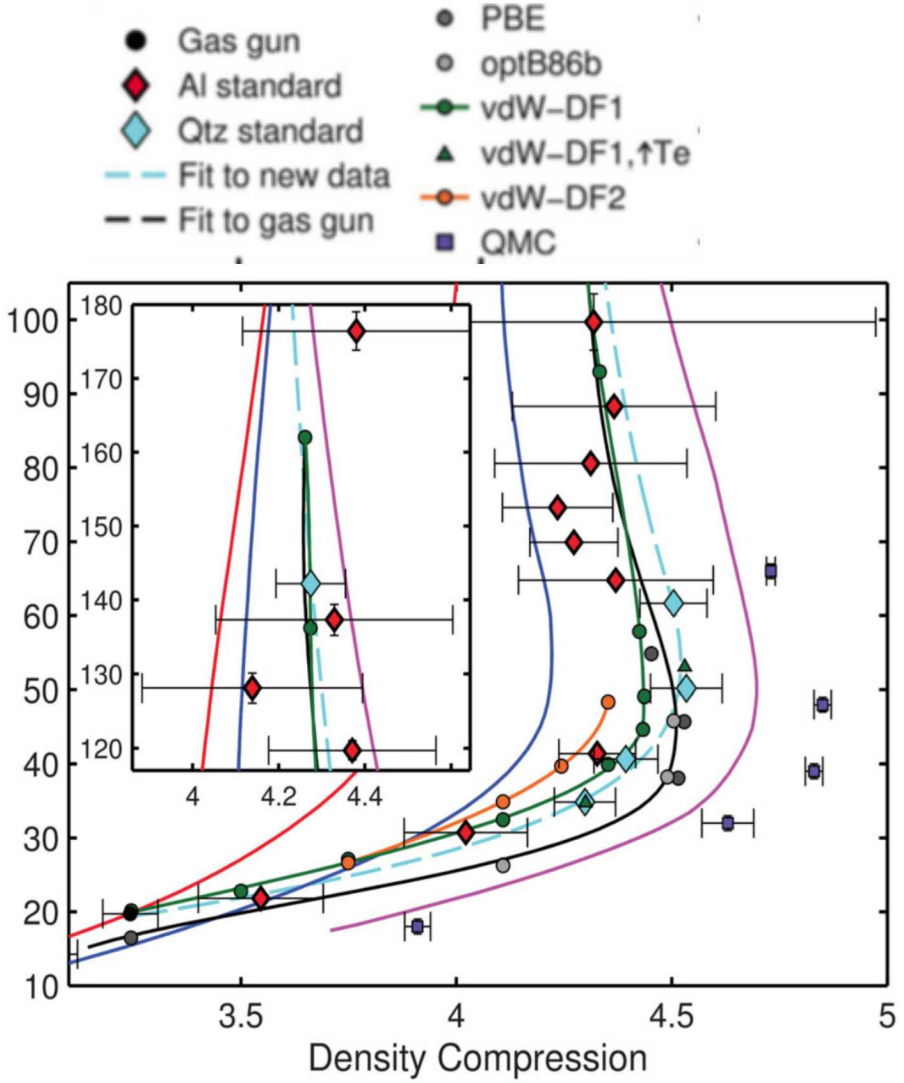
Simple Beyond-Single Slater-Jastrow Trial Wavefunctions are not a panacea

Lattice Distortion for FeO with **beyond** Slater-Jastrow Trial Wavefunctions



Look at a much more tractable system – D_2 Hugoniot

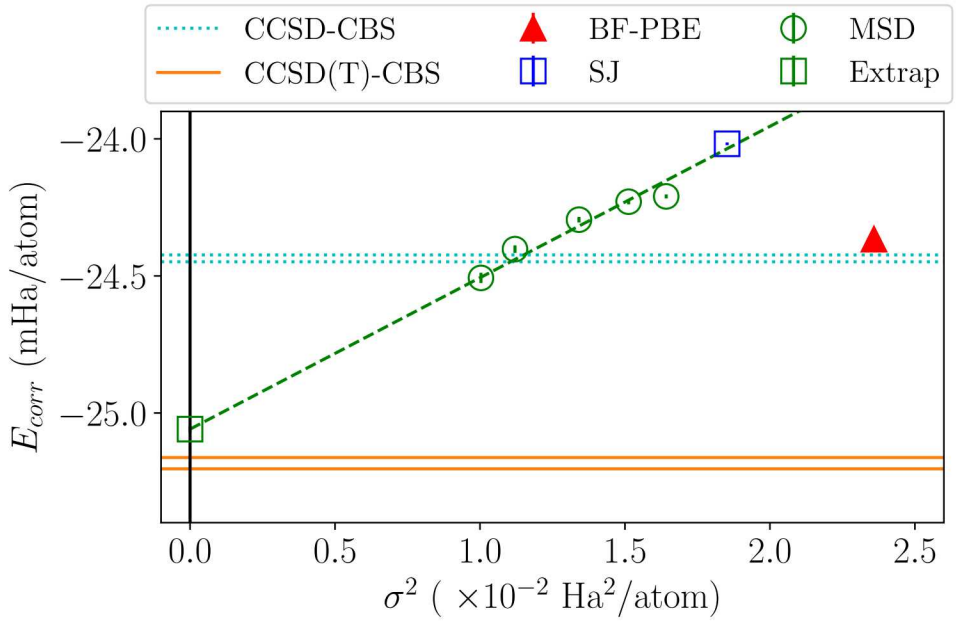
- Coupled electron-ion calculation of Hugoniot
- Significantly more compressible than experiment
- This includes non-controversial gas gun experiments
- With DFT either there is good agreement or we switch functional to try to better match experiment
- With QMC we can try to improve the approximation directly

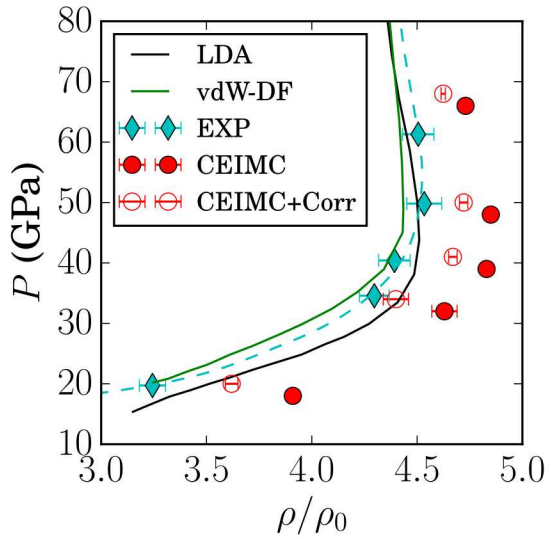


Knudson and Desjarlais, PRL **118**, 035501 (2017)

Tubman, Liberatore, Pierleoni, Holzmann, and Ceperley Phys. Rev. Lett. **115**, 045301

First steps towards systematic improvability





We can go further in a simpler system

Choose small representative snapshots from high pressure liquid deuterium and enumerate and variationally optimize a large multideterminant expansion

Systematically improvable multideterminant wavefunctions allow errors to be controlled

Analyzed how errors in energy and pressure affected previous results

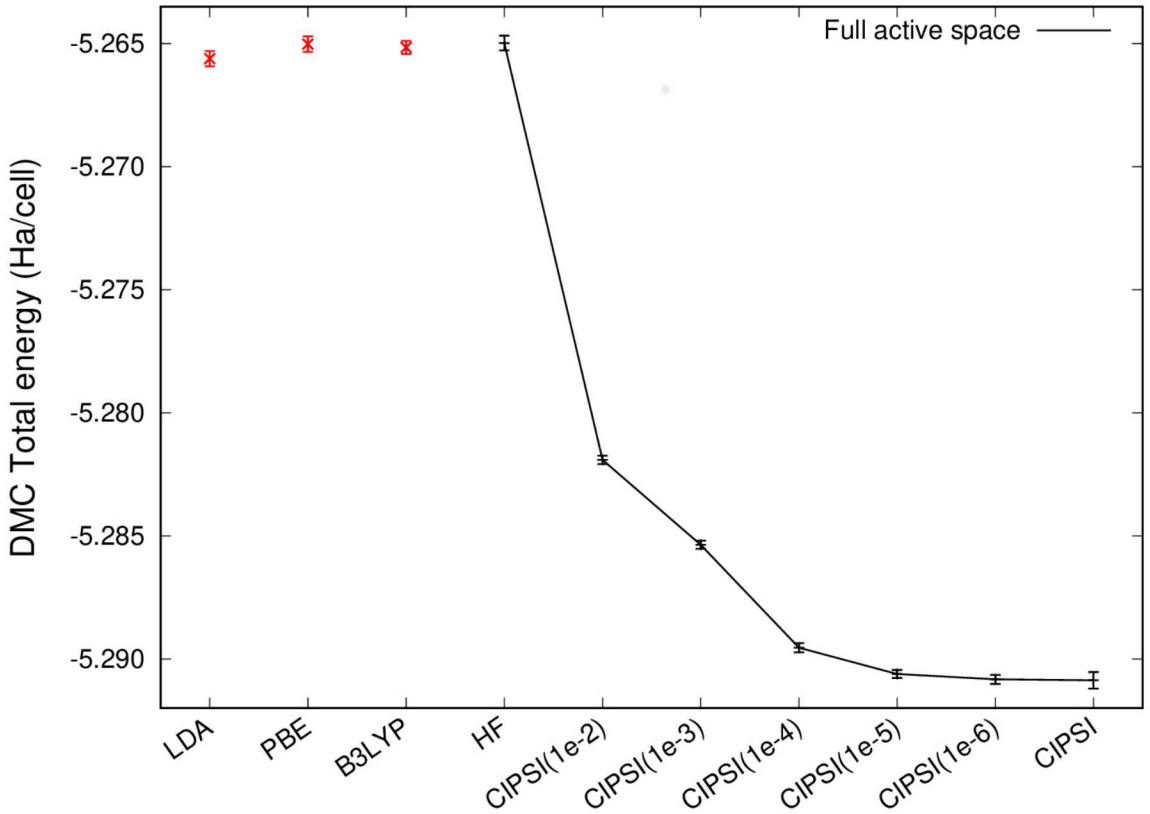
- responsible for significant portion of discrepancy with experiment

Systematic improvement is more important (and feasible) than eliminating all errors

Next step is to be much smarter about selecting trial wavefunctions

Leverage recent resurgence in methods to approximate CI by perturbatively selecting determinants

For example try carbon diamond primitive cell



1. Define a reference wave function:

$$|\Psi\rangle = \sum_{i \epsilon D} c_i \, |i\rangle \qquad Evar = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

2. Generate external Determinants

   All single and double excitations

3. Second order perturbative contribution of each determinant $|\alpha\rangle$

$$\Delta E = \frac{\langle \Psi | \hat{H} | \alpha \rangle \langle \alpha | \hat{H} | \Psi \rangle}{E_{var} - \langle \alpha | \hat{H} | \alpha \rangle}$$

4. Select $|\alpha\rangle$'s with largest ΔE_α and add them to Determinant space (D)

5. Diagonalize $\hat{H}$ in D then update $|\Psi\rangle$ and E_{var}

6. Iterate until reaching convergence.

How to make this generally practical?

Selective CI based methods are inherently exponential!

However, we can evaluate large expansions relatively inexpensively in QMC

- Leveraging generalization of Sherman-Morrison plus smart tricks, we can evaluate several million determinants for QMC while increasing the cost by only an order of magnitude or so

Still this only gets us to small-ish problems – maybe 10 electrons or so

A few more tricks can often increase this by a few factors

- Smart choices of active space
- Exploitation of symmetries

Truncation	Nb_dets	Energy (Ha)
CIPSI(1e-2)	144	-10.5638 (3)
CIPSI(1e-3)	4367	-10.5707 (3)
CIPSI(1e-4)	76013	-10.5791 (3)
CIPSI(1e-5)	992337	-10.5812 (3)
CIPSI(1e-6)	1666608	-10.5817 (3)
CIPSI	1831452	-10.5817 (7)

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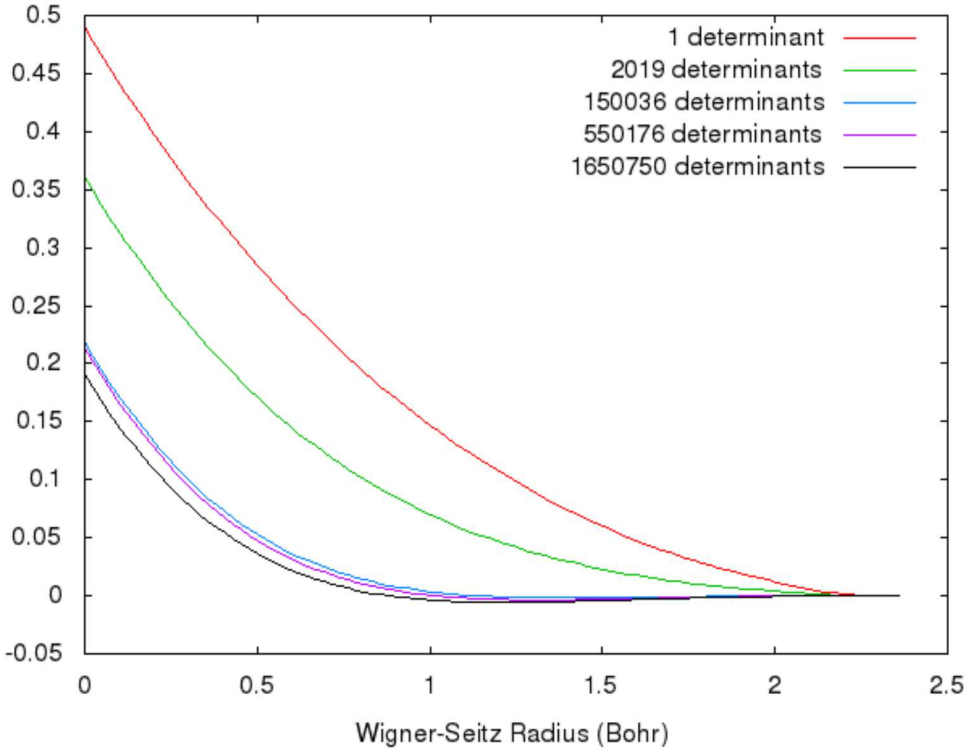
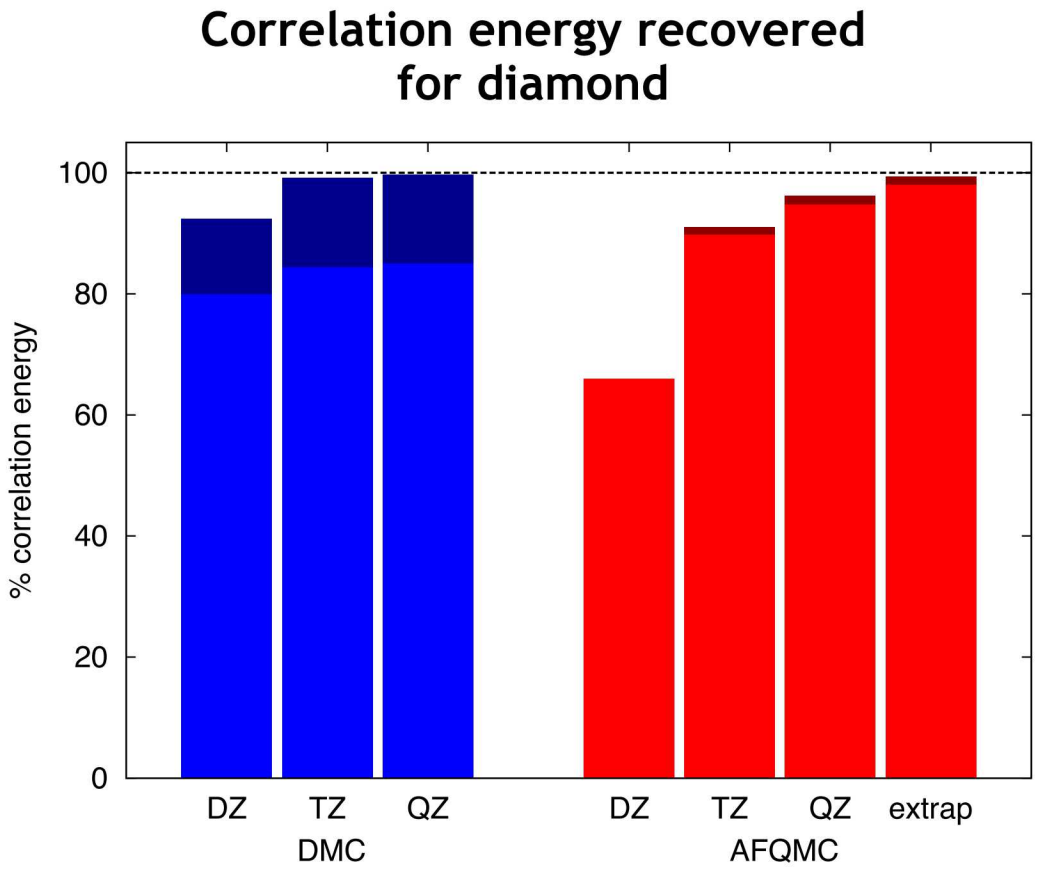
There is much more to be gained, consider for instance the interplay between large expansions and the two body Jastrow factor

Optimized Two-Body Jastrow factor as size of determinant expansion is increased



We are also exploring alterative QMC approaches



Light bars – Single Determinant Trial
Dark Bars – Multideterminant Improvement

Applying two different QMC methods with different classes of approximation

- Should agree if approximations are made arbitrarily small

Learn from comparison about strengths and weaknesses of the methods and how to improve them going forward

Note: QMCPACK now contains a highly optimized AFQMC implementation (qmcpack.org)

Real vs Orbital Space Comparison so far

DMC

- Trivial explicit correlation
  - Jastrow is almost free!
- Generally more accurate trial wavefunctions
  - Led to sophisticated optimization techniques
- No basis set extrapolation. Works at CBS limit.
- Memory friendly
- Intuitive
- Relatively large community, approximations relatively well understood

AFQMC

- Direct connection between ab-initio and model Hamiltonians
- Flexible treatment of core electrons
  - All-e, frozen-core, ECP, NCPP, etc.
- Spin-orbit coupling is easy to incorporate
- Typically smaller bias from phaseless approximation
- Efficient/simple code
  - GEMM, QR, Inverse

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- Hard to simplify
- Pseudopotential approximations introduce additional difficult to control dependence on trial wavefunction
- Fixed-node error is larger
  - Often relying on error cancellation
- Spin orbit as relatively more difficult
- Divergent potentials
  - Observables like forces are noisier

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- Smaller ab-initio community
- Basis set error
  - Error cancellation is “transferred to the basis”
- Requires 2-electron integrals
  - M^{2-3} memory cost
- No direct algorithm
- Forces require xN_{atoms} more memory
- Larger mixed estimator bias

Pseudopotentials have also been identified as a major potential source of error

For accurate calculations of functional materials (e.g. perovskites), explicitly correlated methods like QMC need to be solving the *correct* Hamiltonian.

Effective Core Potentials (ECPs) are necessary in order to feasibly tackle large systems, include relativity, etc.

We envision constructing a new generation of pseudopotentials that are highly accurate and isospectral to the original many-body Hamiltonian:

→ Many-body construction. Constructed from relativistic *many-body* spectra leading to the reproduction of *nearly exact* many-body properties.

→ Reliable and universal. Tested and validated in many-body framework. Usable in both mean-field and many-body methods (in the spirit of the original all-electron *H*)

Many-body spectra and norm-conservation

Total objective function

$O^2 = \omega_0 \mathcal{E}^2 + \omega_1 \mathrm{N}^2$

CCSD(T) energy consistency:

$\mathcal{E}^2 = \sum_s (\Delta E_s^{ECP} - \Delta E_s^{AE})^2$, note that for elements we have worked on ΔE_s^{AE} agrees with experiment to 0.03 eV

Norm-conservation:

$$\mathrm{N}^2 = \sum_l \left(N_l^{ECP} - N_l^{AE}\right)^2 + \left(V_l^{ECP} - V_l^{AE}\right)^2 + \left(S_l^{ECP} - S_l^{AE}\right)^2 + \left(\varepsilon_l^{ECP} - \varepsilon_l^{AE}\right)^2$$

Where N_l is the norm inside a cutoff radius, V_l, S_l, ε_l: value, derivative and eigenvalue of the orbital

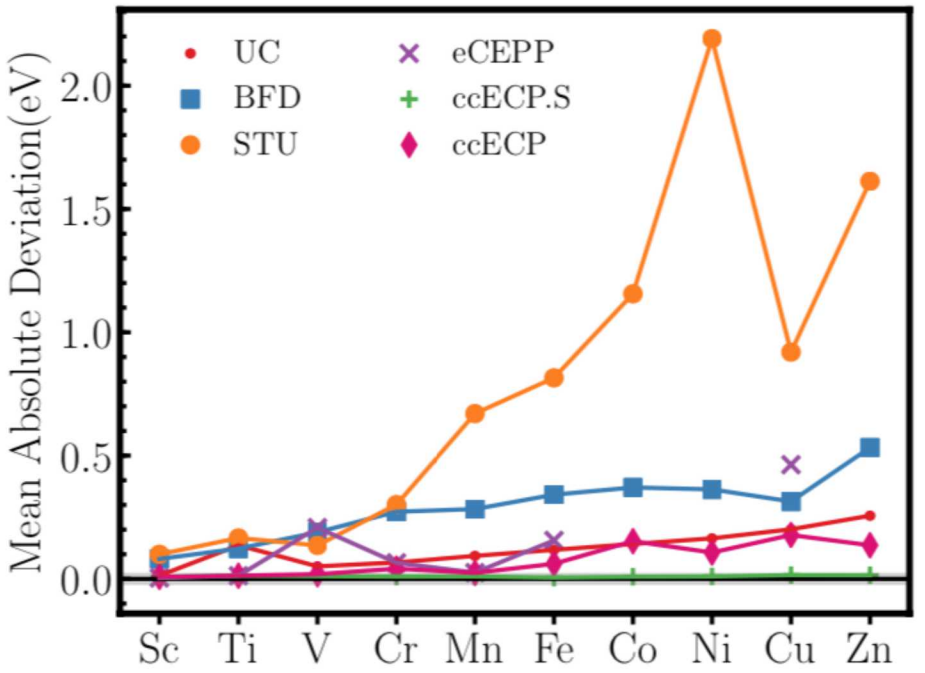
What does this buy us?

Example Spectrum (Ni)

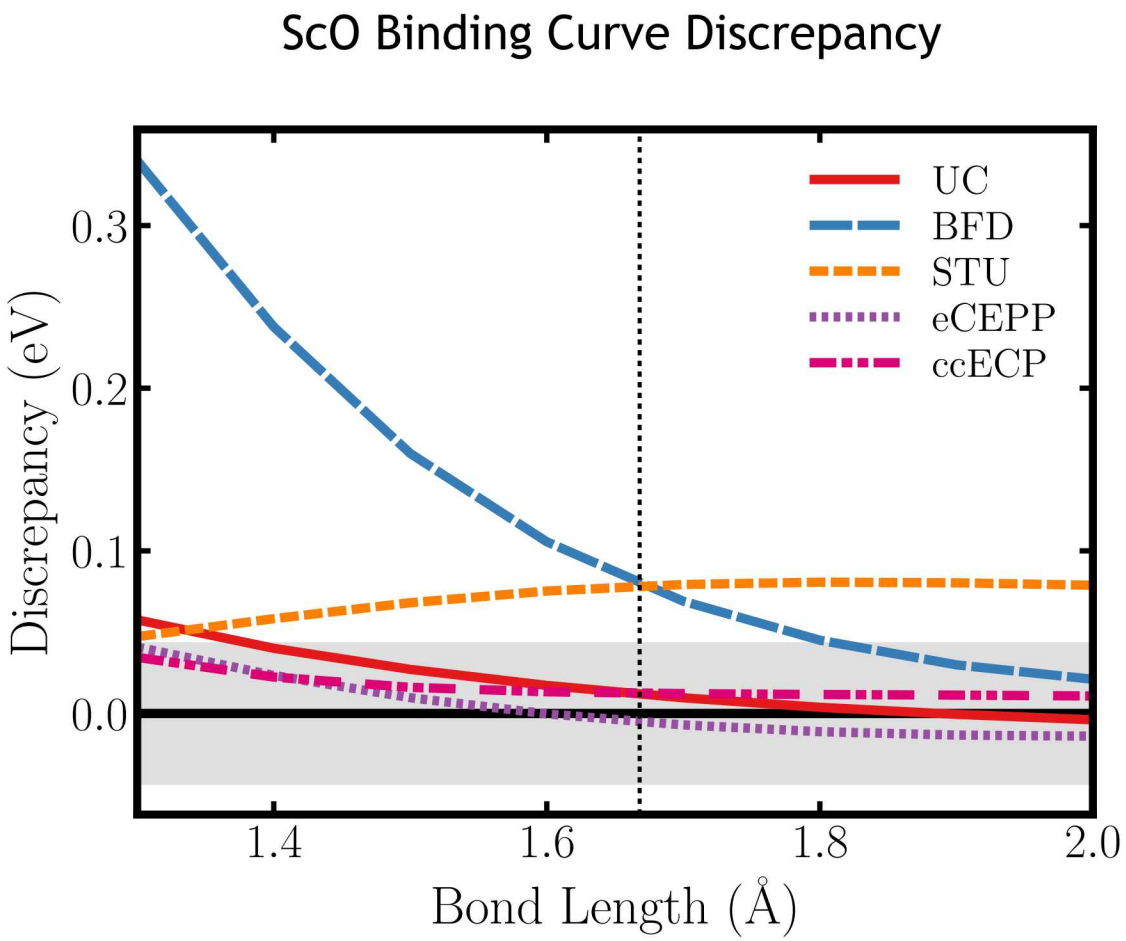
[Ar] $3d^8 4s^2$	^3F	[Ar] $3d^5$	^6S
[Ar] $3d^9 4s^1$	^3D	[Ar] $3d^4$	^5D
[Ar] $3d^{10}$	^1S	[Ar] $3d^3$	^4F
[Ar] $3d^8 4s^1$	^4F	[Ar] $3d^2$	^3F
[Ar] $3d^9$	^2D	[Ar] $3d^1$	^2D
[Ar] $3d^8$	^3F	[Ar]	^1S
[Ar] $3d^7$	^4F	[Ne] $3s^2$	^1S
[Ar] $3d^6$	^5D	[Ar] $3d^9 4s^2$	^2D

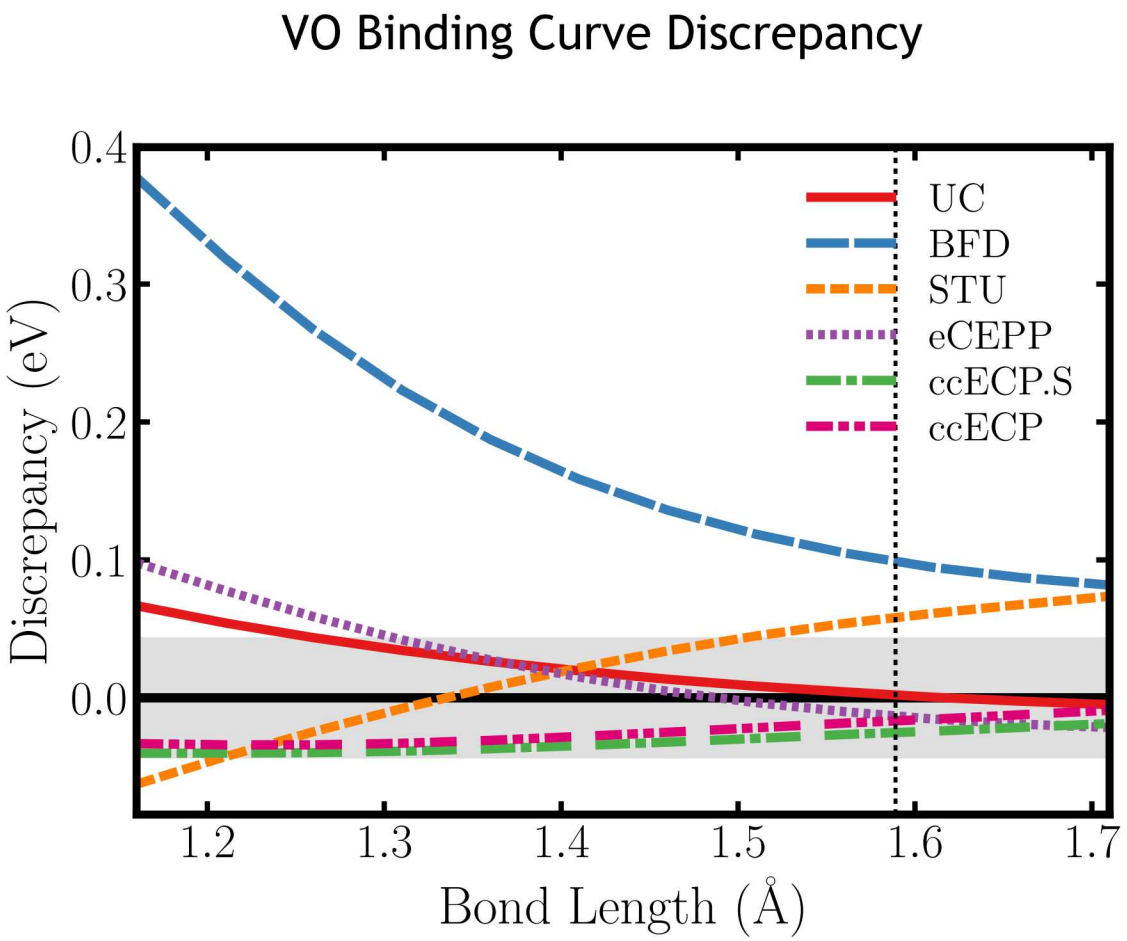
Mean Absolute Deviation:

$$\frac{1}{N}\sum_{s=1}^{N}\left|\left(E_s^{\mathrm{PP}}-E_{\mathrm{GS}}^{\mathrm{PP}}\right)-\left(E_s^{\mathrm{AE}}-E_{GS}^{\mathrm{AE}}\right)\right|$$



Example of transferability





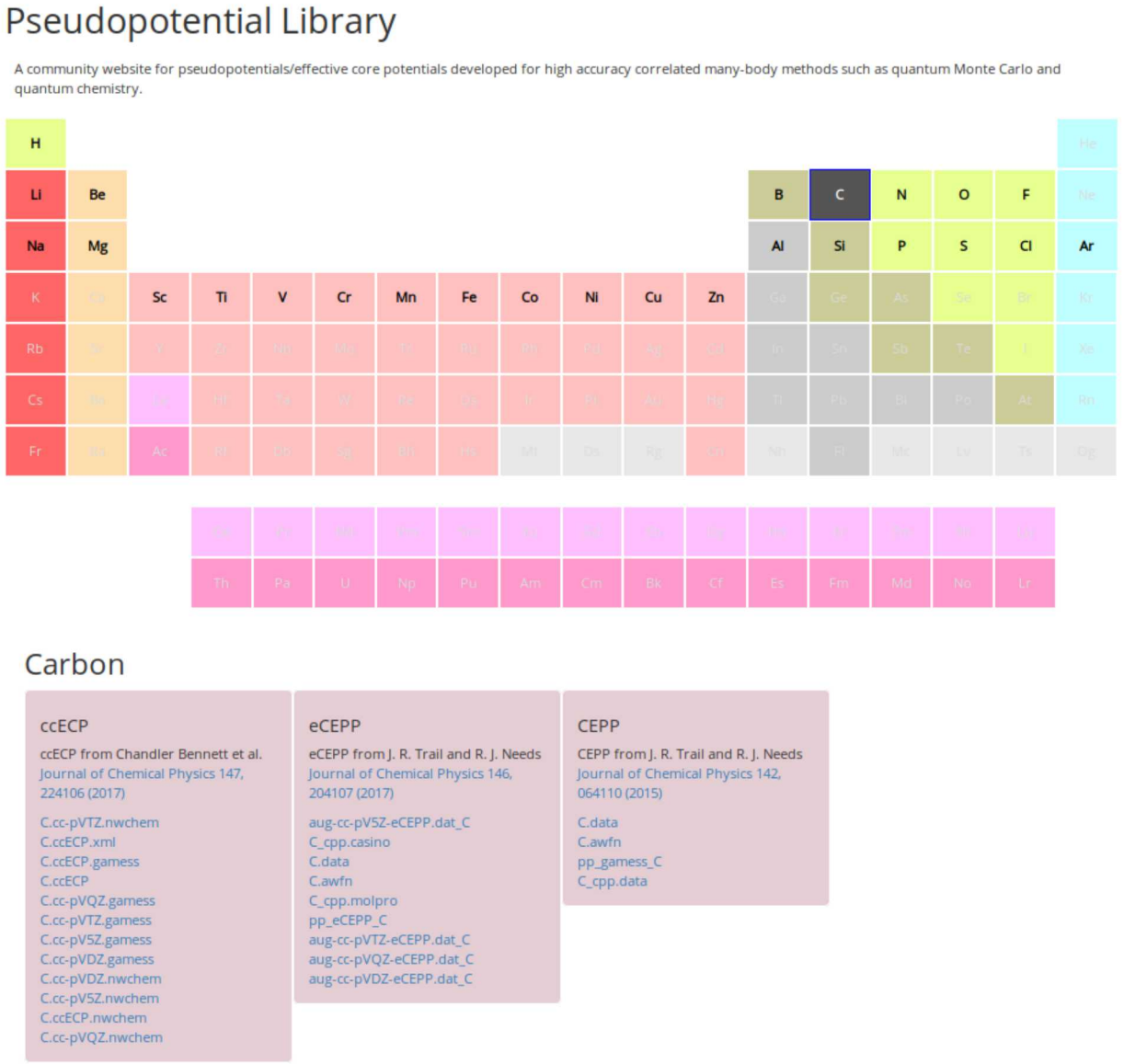
These potentials (and others) are freely available

Pseudopotentiallibrary.org

Includes these potentials as well as others meant to be used in many-body calculations

Coverage of the periodic table is continually expanding

Would like to eventually include many body testing results with potentials



Beyond the ground state

Work by Neuscamman and collaborators on methods targeting excited state optimization in Variational Monte Carlo

Minimize $\Omega(\omega, \Psi) = \dfrac{\langle \Psi | \omega - \hat{H} | \Psi \rangle}{\langle \Psi | (\omega - \hat{H})^2 | \Psi \rangle}$

Allows a variational state specific optimization algorithm that is size extensive and balanced between various states

Shea and Neuscamman, JCTC 13, 6078 (2017)

Targeting Excited States: Gaps

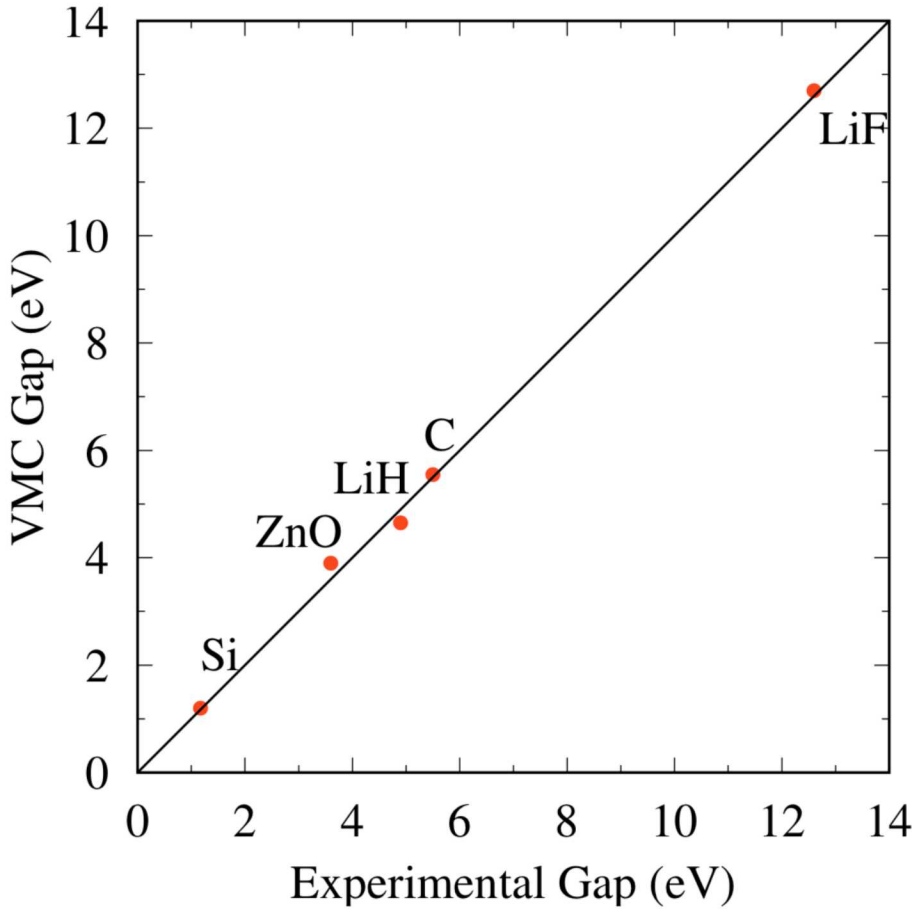
Variational optimization of multi-Slater Jastrow trial wavefunction

Ground state optimizes all single particle-hole excitations

Excited state includes most single and double particle hole excitations

- Actually for efficiency include only double excitations from singles with relatively large contribution

MAD of 3.5%

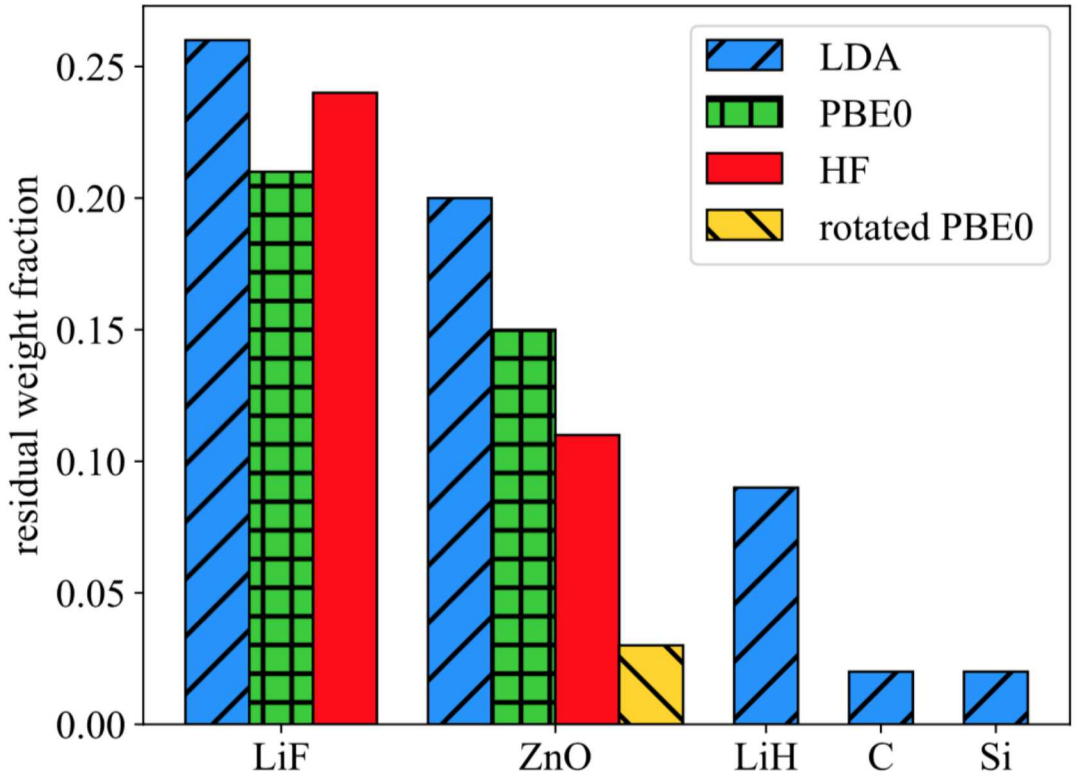


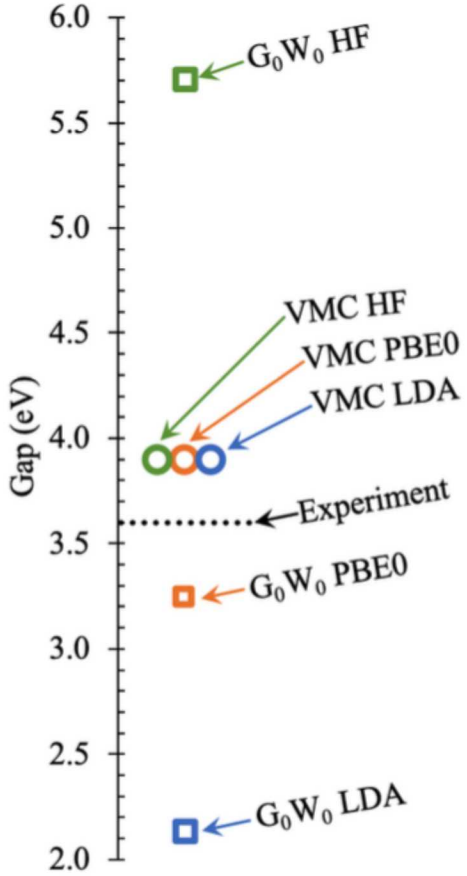
Zhao and Neuscamman
Submitted to PRL

Use of VMC allows understanding of results

Investigate choice of single particle basis to feed into MBPT

Sum of squares of CI coefficients other than at valence band maximum and conduction band minimum





Have made progress towards systematically improvable calculations on oxides with QMC

We are expanding scope and improving robustness of QMC with multideterminant trial wavefunctions

- Also exploring orbital space vs continuous approaches

Have produced a series of accurate pseudopotentials designed for many-body calculations

Are using these new capabilities to start adding to our understanding of materials and also other computational methods