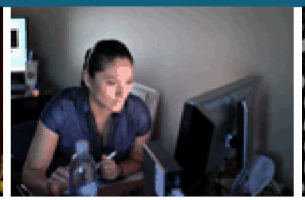
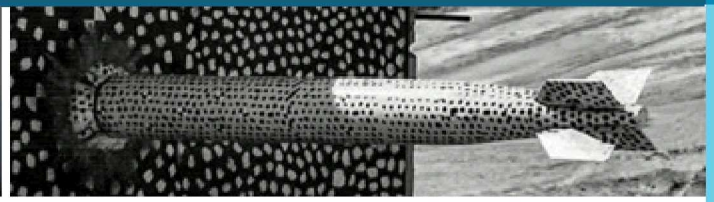
SAND2020-2994C

Accurate Calculations of a Solid State Test Set with Quantum Monte Carlo Methods





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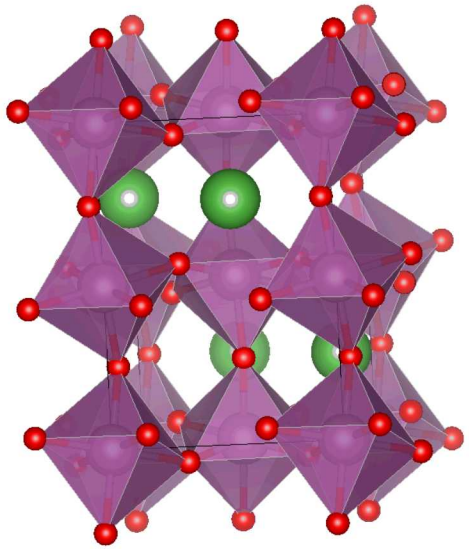
Motivation



Accurate predictions for the properties of functional materials requires accurate *ab-initio* solutions to the many-body Schrödinger equation

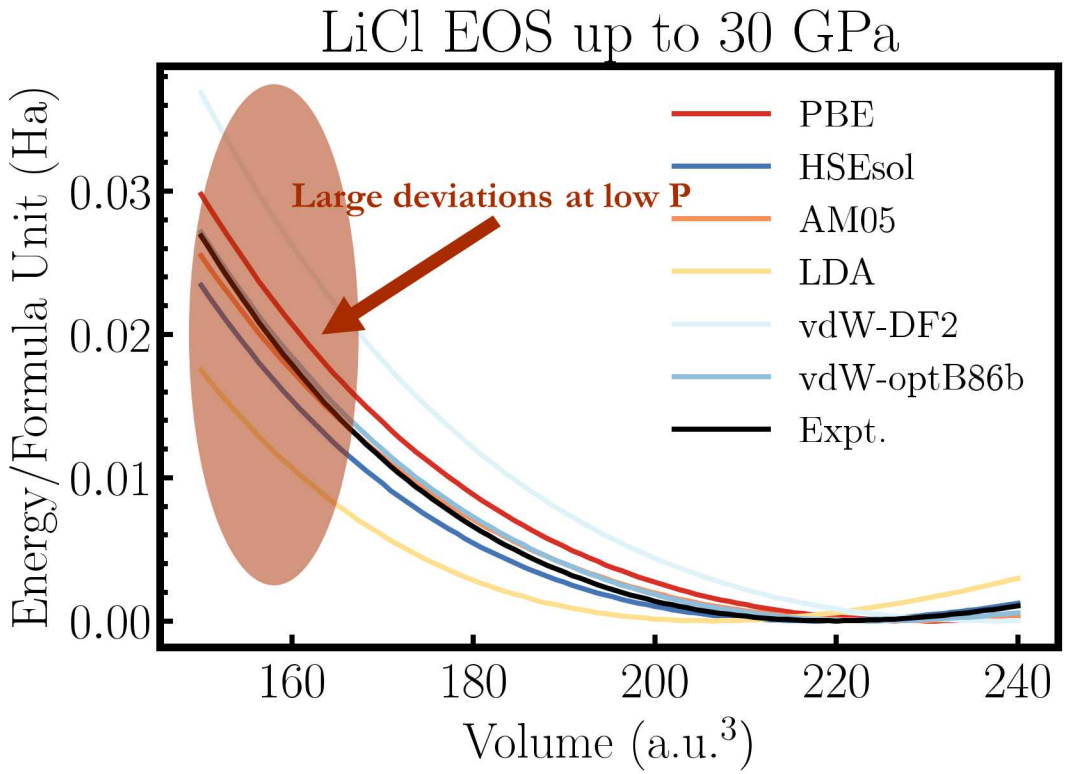
$$\left(\hat{T} + \hat{V}_{\mathrm{Ion-Ion}} + \hat{V}_{\mathrm{Elec-Ion}} + \hat{V}_{\mathrm{Elec-Elec}}\right)|\Psi\rangle = E|\Psi\rangle$$

Properties: Cohesion, Optical Properties (gaps), Magnetic Phases, Structural Phase Transitions, etc.

Density Functional Theory (DFT) has been the method of choice due to its cheap computational cost and reasonable accuracy across many systems and scales.

EOS (T=0K) is one of the simplest metrics for measuring the accuracy of an electronic structure method.

Even for simple systems, various DFT can produce vastly large errors in the EOS, especially at high pressure!

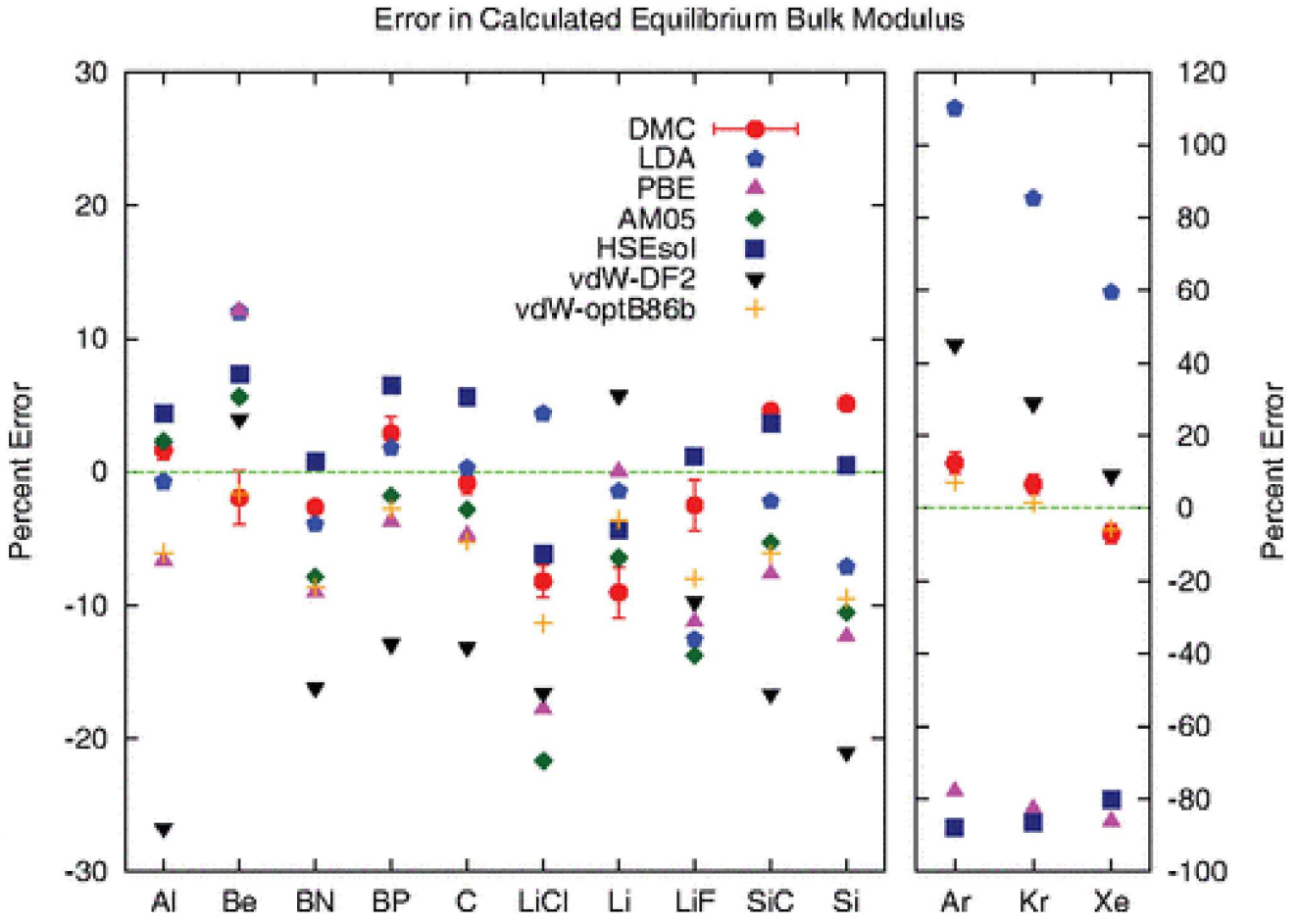


Solid State Test Set and Previous Results

- Test set for EOS probes a variety of simple solids with various types of bonding…ionic, covalent, metallic, and vdW
- Various DFT have MARE(%) ranging from 6%-26% error from expt.
- Previous state-of-the-art DMC makes overall improvement 5% MARE (%). Still room for improvement

$$E(V) = E_0 + \frac{2B_0V_0}{(B_0'-1)^2}\left[2 - \left(5 + 3\left(\frac{V}{V_0}\right)^{1/3}(B_0'-1) - 3B_0'\right)\right] \times \exp\left(-\frac{3}{2}(B_0'-1)\left[\left(\frac{V}{V_0}\right)^{1/3} - 1\right]\right)$$

We revisit the test set using Diffusion Monte Carlo (DMC) and Auxiliary Field QMC (AFQMC), utilizing recent methodological advances to show improved accuracy of EOS



Shulenburger & Mattsson, PRB **88**, 245117 (2013)

Methodology

DMC and AFQMC both utilize imaginary time propagation from an initial Ψ_T to obtain *accurate* and *explicitly correlated* energies

$$|\Psi_0\rangle \propto \lim_{\tau\to\infty} \exp\left[-\tau\mathcal{H}\right]|\Psi_T\rangle$$

$$E_0 = \lim_{\tau\to\infty} \frac{\langle\Psi(\tau)|\mathcal{H}|\Psi_T\rangle}{\langle\Psi(\tau)|\Psi_T\rangle}$$

Diffusion Monte Carlo

- 1st Quantization: Samples Configuration Space

$$\langle\mathbf{R}'|\Psi^{(n+1)}\rangle = \int d\mathbf{R} G(\mathbf{R}\to\mathbf{R}';\tau)\langle\mathbf{R}|\Psi^{(n)}\rangle$$

- Fixed-Node Approximation to deal with FSP
- FN is typically largest bias

Auxilary Field QMC

- 2nd Quantization: Samples Determinant Space

$$|\Psi^{(n+1)}\rangle = \int d\mathbf{x}\, p(\mathbf{x})\hat{B}(\mathbf{x})|\Psi^{(n)}\rangle$$

- Phaseless Approximation to deal with FSP
- Bias is smaller, but has large basis set errors

Session F40.00010: DMC vs. AFQMC systematically improved Ψ_T and exact energies

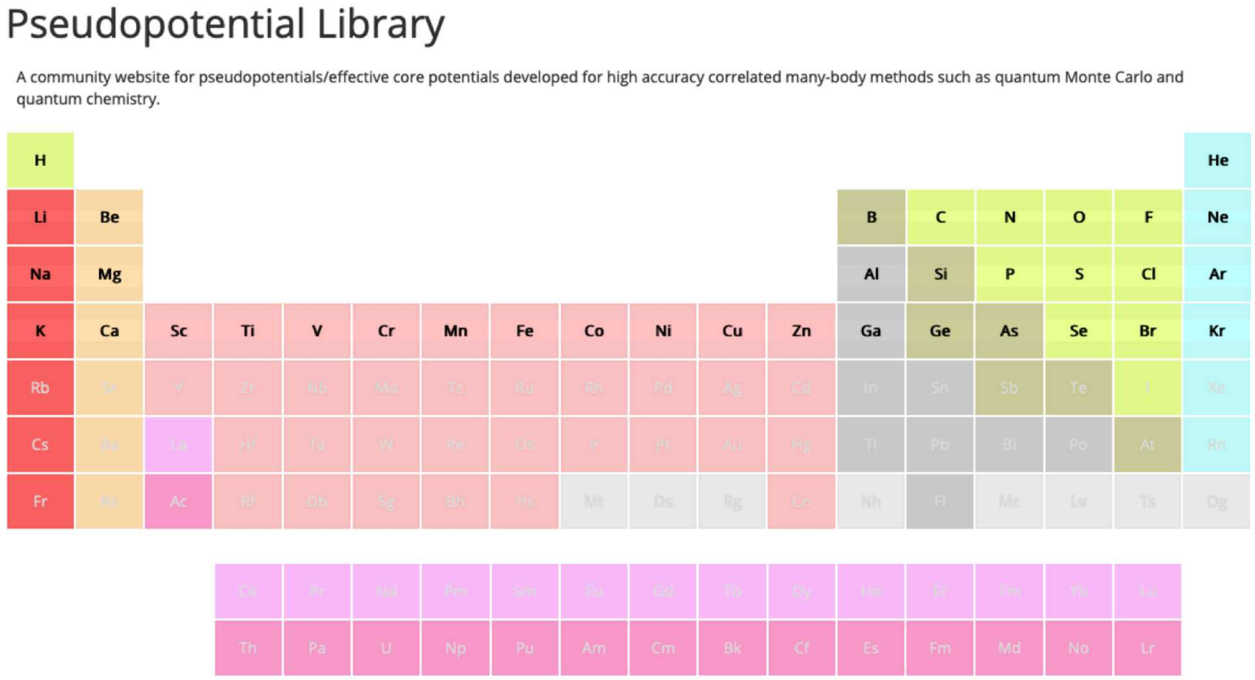
QMCPACK

All calculations driven by NEXUS. This workflow script will be released as a **reference workflow** for QMCPack. This will be used for future reproducibility, testing of methodological advances, and as a tutorial script for new users.

- All Ψ_T come use PBE orbitals from Quantum Espresso. DMC has 1,2,3 body J
- Time-step bias controlled by extrapolation
- One-body FS effects controlled via twist-averaging
- Two-body FS effects corrected with various schemes (e.g. KZK, $S(k)$, Chiesa, etc.)

Large source of uncertainty in previous DMC came from inaccurate ECPs.

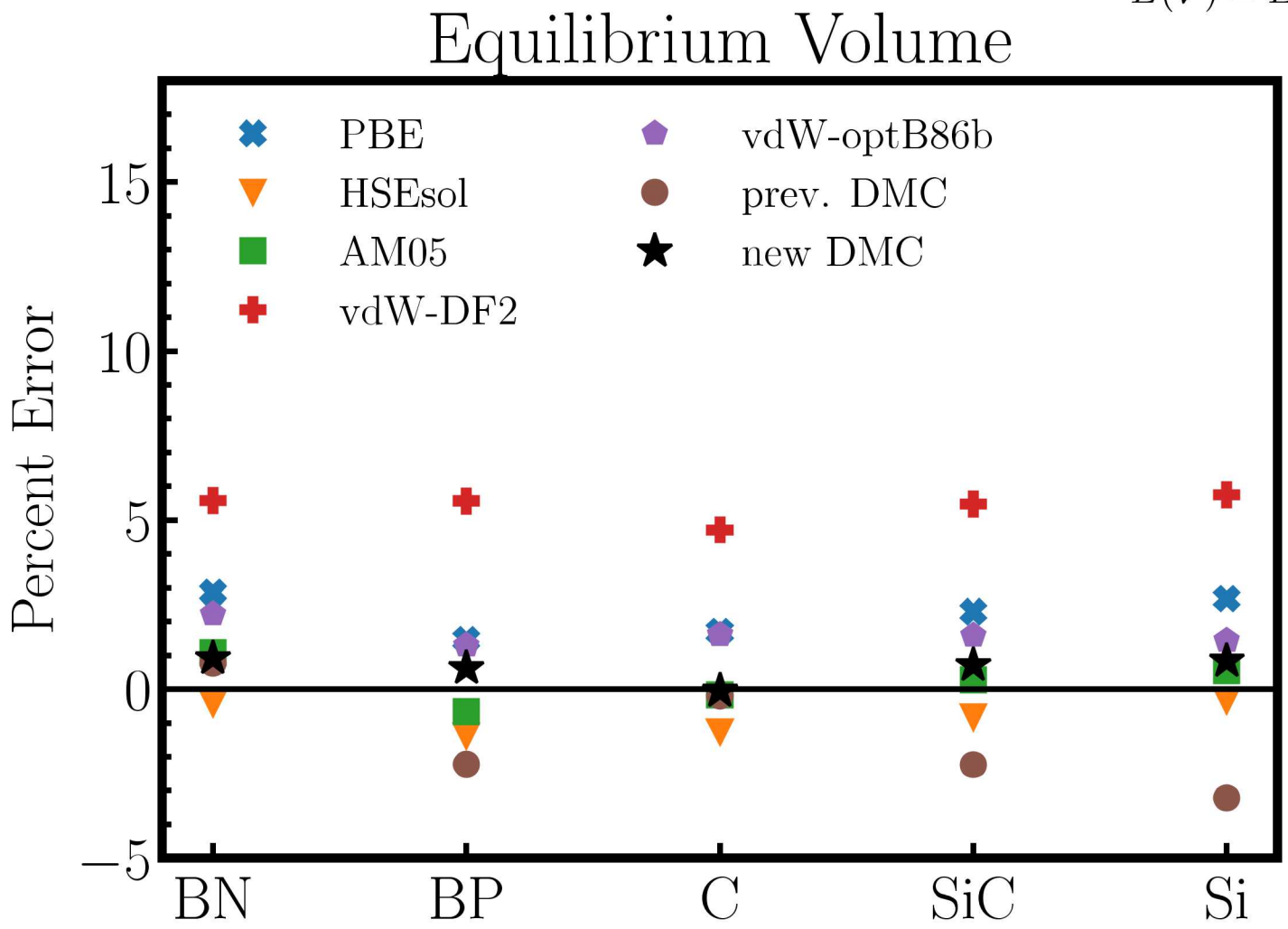
Here, we improve upon previous DMC by utilizing recent *explicitly correlated ECPs* designed for many-body calculations



http://pseudopotentiallibrary.org/

Preliminary DMC Results

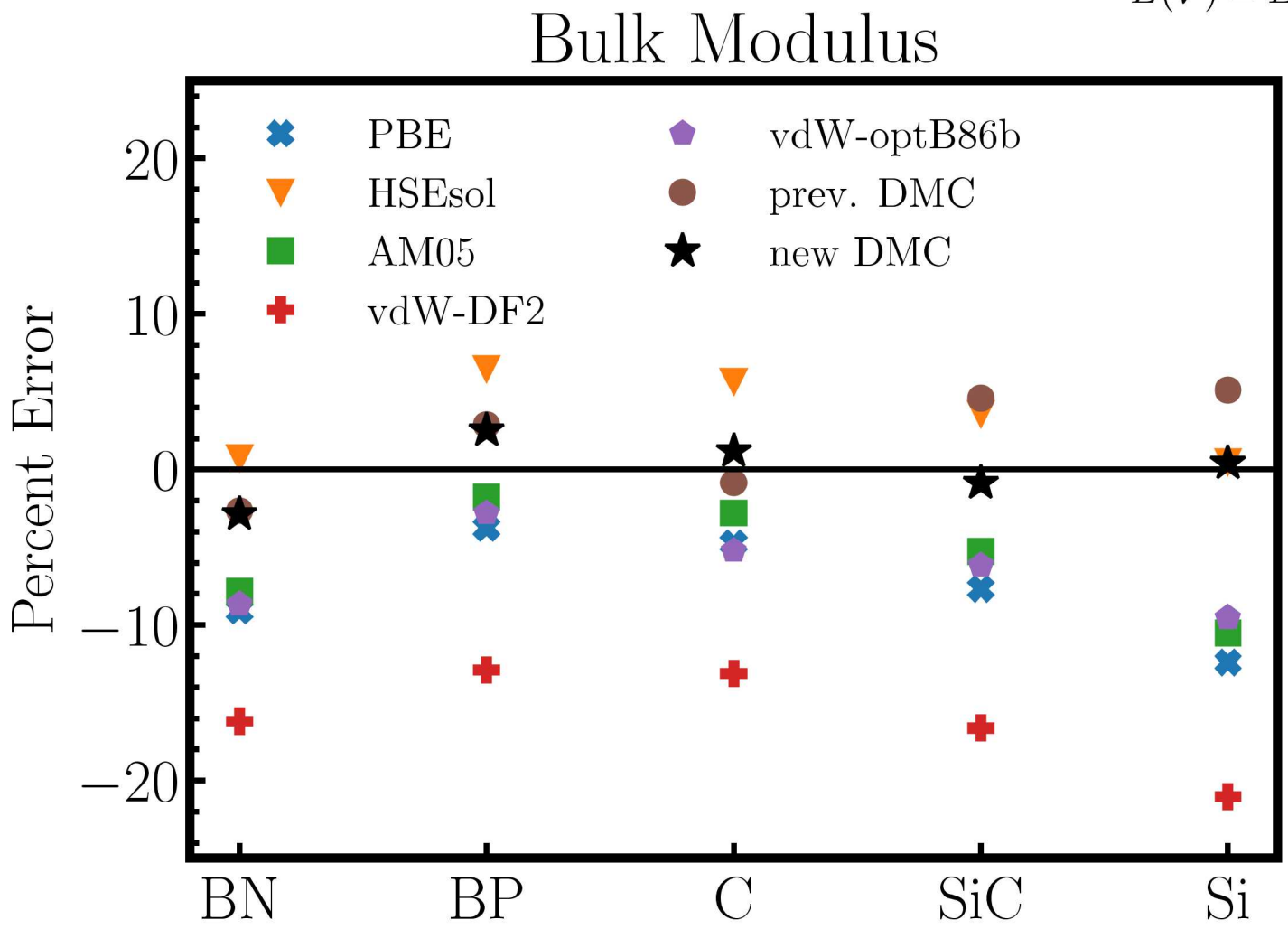
$$E(V) = E_0 + \frac{2B_0V_0}{(B_0'-1)^2}\left[2 - \left(5 + 3\left(\frac{V}{V_0}\right)^{1/3}(B_0'-1) - 3B_0'\right)\right] \times \exp\left(-\frac{3}{2}(B_0'-1)\left[\left(\frac{V}{V_0}\right)^{1/3} - 1\right]\right)$$



- Previous DFTs up to 5% MARE for this subset
- MARE(%):
  Old DMC: 1.8 New DMC: 0.6
- **Using more accurate ECPs leads to 3x reduction in MARE**

Preliminary DMC Results

$$E(V) = E_0 + \frac{2B_0V_0}{(B_0'-1)^2}\left[2 - \left(5 + 3\left(\frac{V}{V_0}\right)^{1/3}(B_0'-1) - 3B_0'\right)\right] \times \exp\left(-\frac{3}{2}(B_0'-1)\left[\left(\frac{V}{V_0}\right)^{1/3} - 1\right]\right)$$



- Previous DFTs up to 15% MARE for this subset
- MARE(%)
  Old DMC: 3.2 **New DMC: 1.5**
- **Using more accurate ECPs leads to 2x reduction in MARE**

Conclusions

- Factor of +2x improvement to EOS by using correlated ECPs in QMC calculations
- Finite-size correction schemes allow for accurate EOS without needing large supercells or costly extrapolations
- Nexus workflow to be released as a reference to reproduce all work, test future methodological advances, learning script, etc.

To Do:

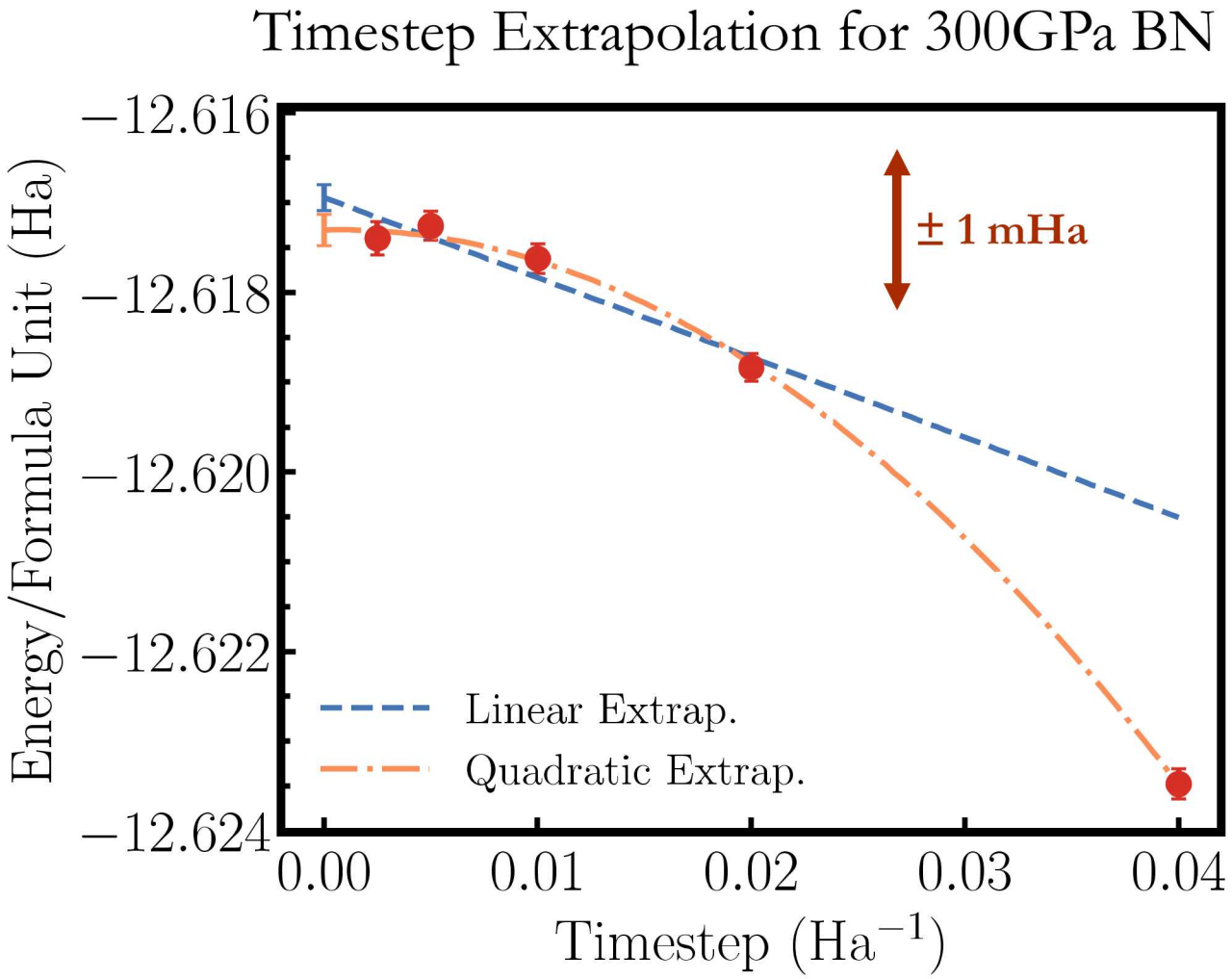
- AFQMC cold curves still ongoing
- Investigate more sophisticated KE corrections (long ranged Jastrow corrections from Holzmann *et al.*, PRB **94**, 035126 (2016)
- FS corrections for AFQMC, basis set corrections AFQMC, comparison of DMC to AFQMC

Backup: Timestep Bias

Both DMC and AFQMC use a Trotter decomposition to approximate the imaginary-time projector

For each system, we perform a timestep extrapolation of energies at 300GPa and ambient conditions to converge energy to <1 mHa/Formula Unit

In each system and method, we find a 0.01 Ha^{-1} was sufficient for convergence. This is used for the entire $E(V)$ curve.



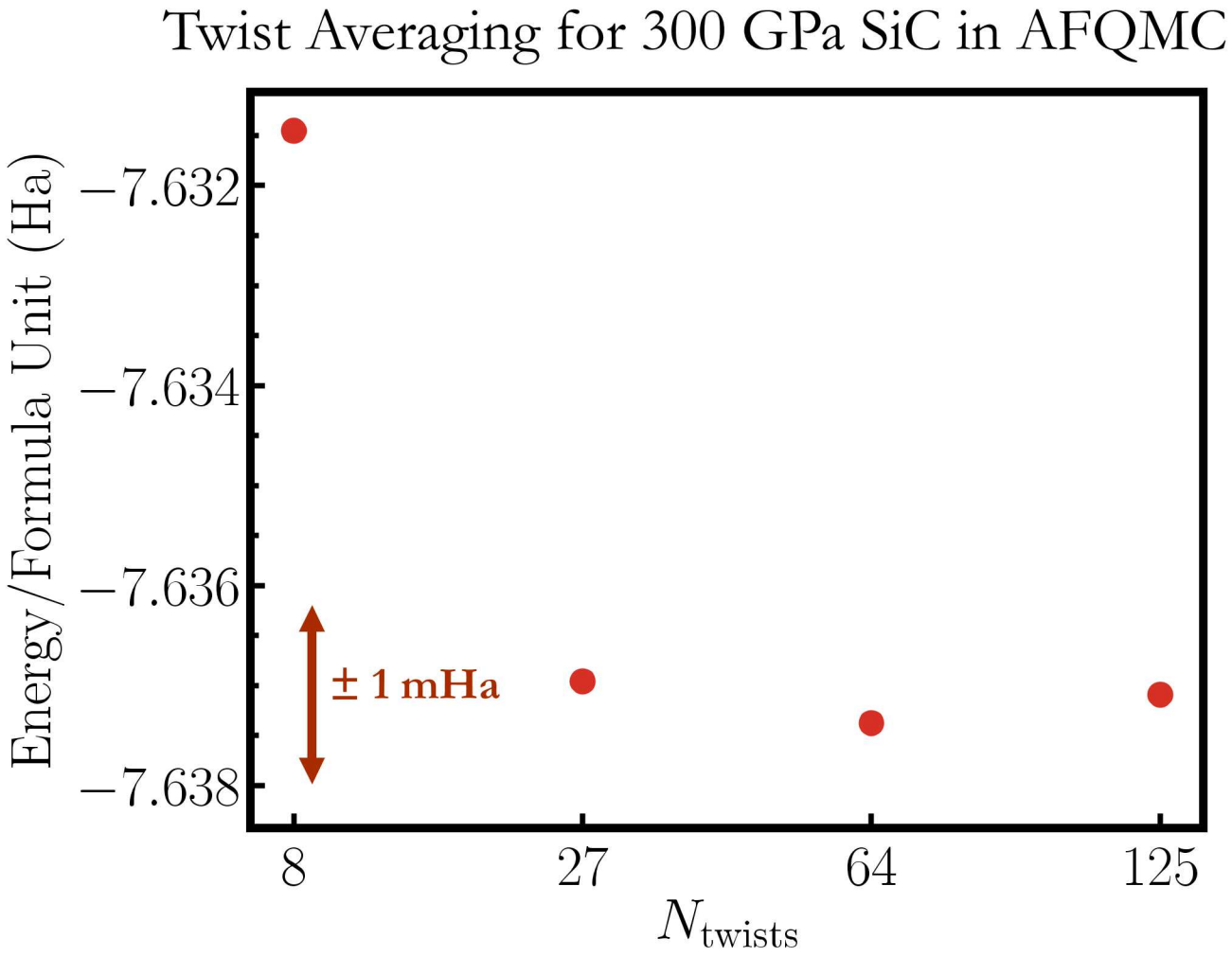
Backup: One-Body Finite-Size Bias

1b FS effects are dominated by shell effects, sub-leading order come from long-range behavior of Jastrow

Leading order corrections are addressed by twist-averaging. Similar to BZ sampling in DFT.

$$E_{\mathrm{TA}} = \frac{1}{N_{\mathrm{tw}}} \sum_{\mathbf{k}_s}^{N_{\mathrm{tw}}} E_{\mathrm{QMC}}(\mathbf{k}_s)$$

In each system and method, we find a 4x4x4 twist grid sufficient to converge the energies to <1mHa/Formula Unit.

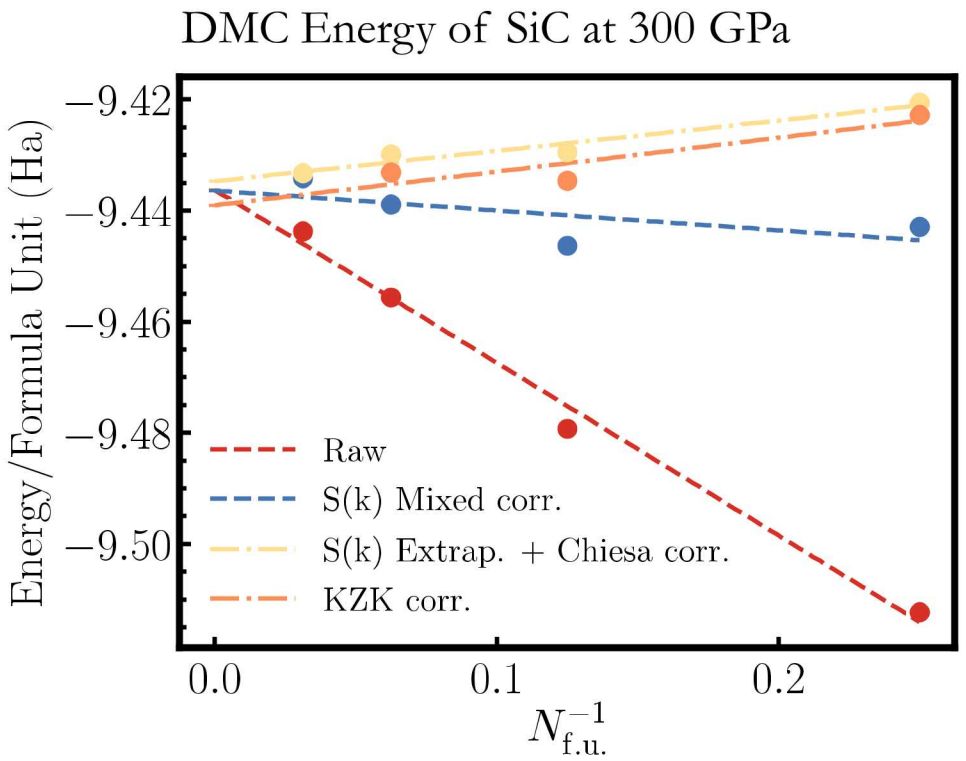


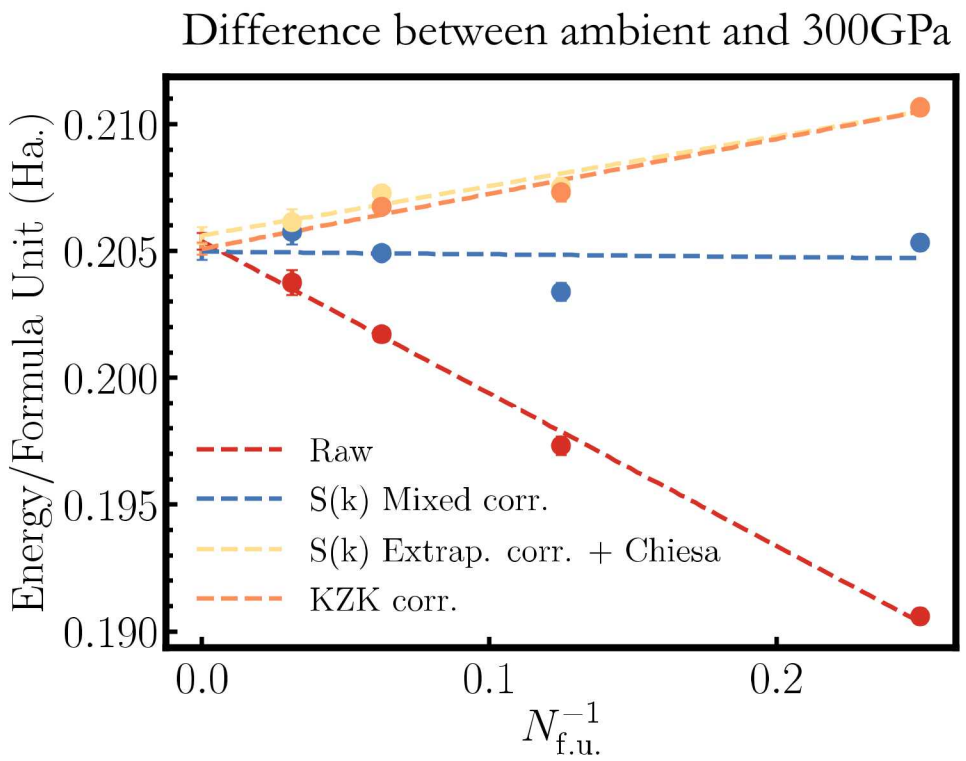
Backup: Two-Body Finite-Size Bias

In a finite simulation cell under PBC, artificial repetition of XC hole introduces large error into the potential (and kinetic) energies…must be extrapolated or corrected.

Simple 1/N extrapolation requires many simulation cells which is costly.

FS corrections: KZK (DFT-based total energy), $S(k)$ (potential energy), Chiesa (kinetic energy)





Backup: AFQMC Basis Set Convergence

Whereas DMC works in $\mathbb{R}^{3N}$ configuration space, AFQMC works in 2nd quantization, i.e. determinant space. Plagued by finite basis set error.

Here, we use Kohn-Sham basis for AFQMC, following Ma *et al.*, PRL **114**, 226401 (2015)

For E(V) curves, interested in converging *relative* energies