Forces, stress, and geometry optimization with Auxiliary Field Quantum Monte Carlo

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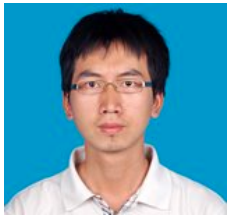

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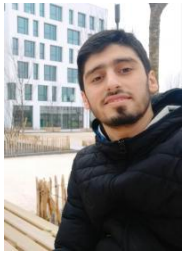

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U.S. DEPARTMENT OF ENERGY

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SIMONS FOUNDATION

Outline

- Motivation
  - ➡ Forces and stresses are important for structural predictions
  - ➡ Beyond DFT (“many-body”) forces and stress are needed, but expensive and difficult
- Fast and accurate force/stress implementation in AFQMC
  - ➡ Benchmark with energy derivatives
- Towards structure predictions: structure optimization
  - ➡ Common algorithms does not interplay well with stochastic AFQMC forces
  - ➡ Our proposed algorithm: FSSD×SET
  - ➡ Full-degree-of-freedom structure optimizations
- Structural properties with AFQMC
  - ➡ Near-exact charge density in solids
  - ➡ Accurate many-body phonon spectrum

Why forces and stresses?

- Structure prediction is an important step in predicting physics
- Optimization needs information about potential energy surface
- With total energy: **slow** (low information density)
- With energy gradients: more efficient prediction of structures

  → **forces** (gradients w.r.t. **ion positions**)

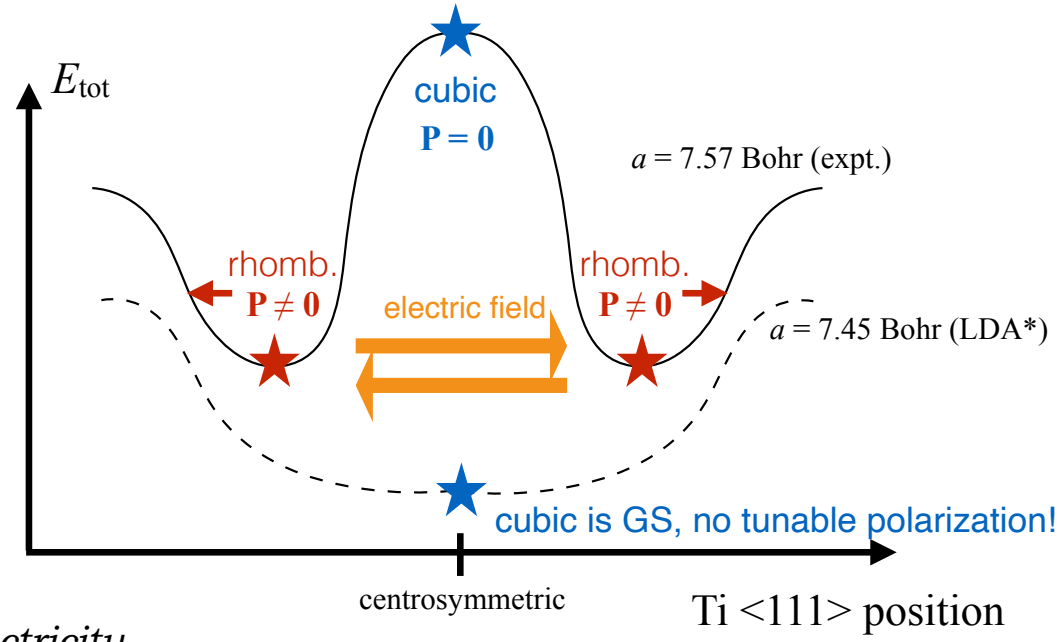
  → **stresses** (gradients w.r.t. **lattice volume / shape**)

Beyond-DFT methods sometimes required

- DFT is an excellent option for computing forces/stresses and relaxing structure
- DFT has accuracy limits (e.g. strongly correlated systems, systems requiring high accuracy)

- Example 1:
  Ferroelectricity in perovskite $BaTiO_3$

*R. E. Cohen and H. Krakauer, *Phys. Rev. B* **42**, 6416 (1990)



- *2% structure error → no ferroelectricity*
- *DFT are sometimes not accurate enough to determine physics*

Beyond-DFT methods sometimes required

- Example 2: Density of ice & water: $\rho = m/V$, $V \leftarrow$ structure (lattice constant)

Table 1. Equilibrium Volume (V) Density (ρ) and Bulk Modulus (B_0) of Cubic (Ic) and Proton-Disordered Hexagonal (Ih) Ice Computed Using Generalized-Gradient (PBE) and Hybrid (PBE0) Density Functionals[a]

ice, method	V/H_2O (Å^3/mol)	ρ (g/mL)	B_0 (GPa)
Ic, PBE	30.50	0.98	14.7
Ih, PBE	30.55	0.98	14.8
Ic, PBE0	31.12	0.96	13.4
Ih, PBE0	31.33	0.95	13.0
expt.	32.03[g]	0.93	8.33[g]–12.1[h]

Table 2. Equilibrium Densities and Compressibilities of Liquid Water Computed Using the PBE and PBE0 Functionals at 400 K with (+D) and without Dispersion–Interaction Corrections (See Text) and Temperature Corrections (+T)[a]

method	density (g/mL)	compressibility (Mbar^{-1})
PBE (160 Ry)[b]	0.81 ± 0.01	69 ± 9
PBE[c]	0.86 ± 0.02	44 ± 7
PBE0[c]	0.71 ± 0.02	108 ± 35
expt.[f]	1.00	45

A.P. Gaiduk, F. Gygi, and G. Galli, *J. Phys. Chem. Lett.* **6**, 2902 (2015)

Computational predictions (PBE/PBE0):

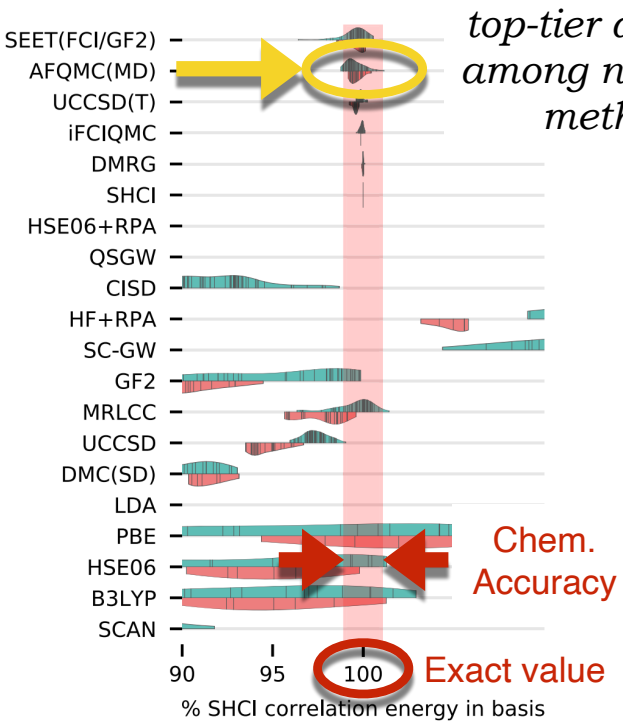
- Ice density = 0.95~0.98 g/mL
  larger than experiment
- Water density = 0.71~0.86 g/mL
  smaller than experiment

- *Ice sinks in water !? → incorrect*
- *"Good" functionals may be inconsistent*
- *Reliable structure predictions need beyond-DFT methods*

Improving the computational method

- "Many-body" (beyond DFT) methods with (near-)exact exchange-correlation
- These methods are often *accurate* but **expensive**, limiting their applications
- Many-body forces have technical challenges and have not been widespread
- Our method AFQMC
  (Auxiliary-field quantum Monte Carlo)
  - ✓ low-scaling $O(N^3\text{-}N^4)$
  - ✓ produces very accurate total energies
  - ✓ direct & accurate forces/stresses possible
  - ➡ *stochasticity (next page)*

Benchmark in transition metal oxides



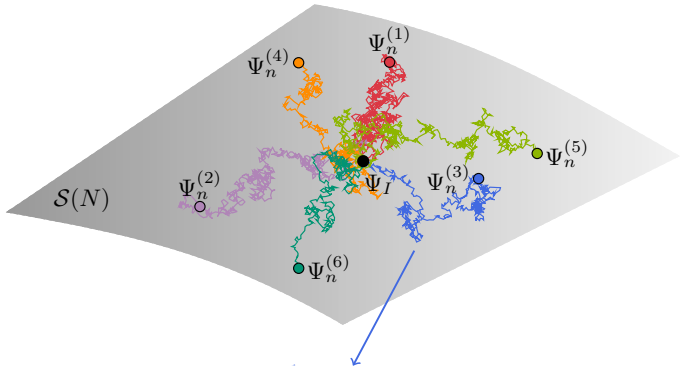
K. T. Williams et al., Phys. Rev. X 10, 011041 (2020)

Stochasticity in AFQMC

Imaginary time propagation

$$|\Psi_T\rangle \xrightarrow{e^{-\beta H}} |\Phi_0\rangle$$

Random walk of Slater determinants

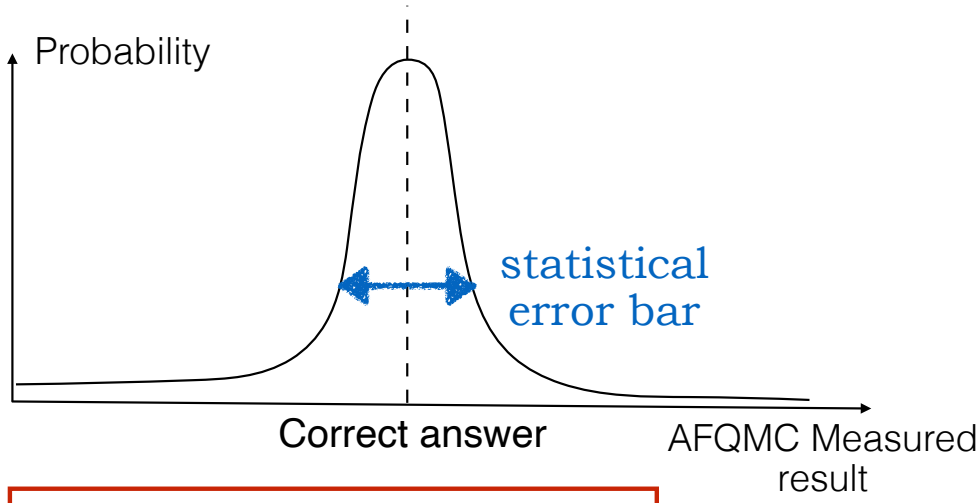


Average of all walkers = many-body wave function

M. Motta & S. Zhang, *WIREs Comput. Mol. Sci.* **8**:e1364 (2018)

Random sampling → features of AFQMC:

- MC is excellent for large Slater det. space dimensions → O(N^3~N^4) scaling
- Results have statistical error



Can be systematically improved with more computations, $\varepsilon \propto C^{-1/2}$

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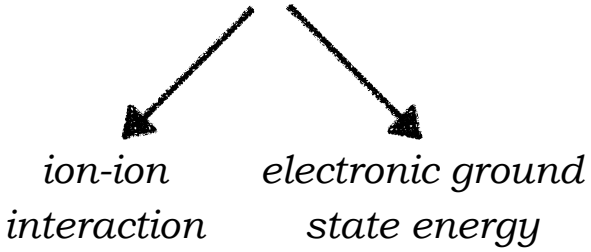
Ionic forces with AFQMC

- Force is derivative of the potential energy to ion positions



- Ion-ion interaction is classical & can be evaluated explicitly

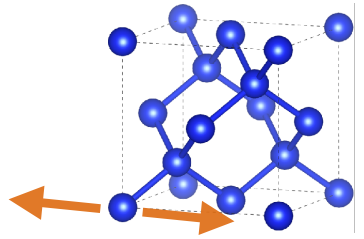
- electronic term: Hellmann-Feynman theorem

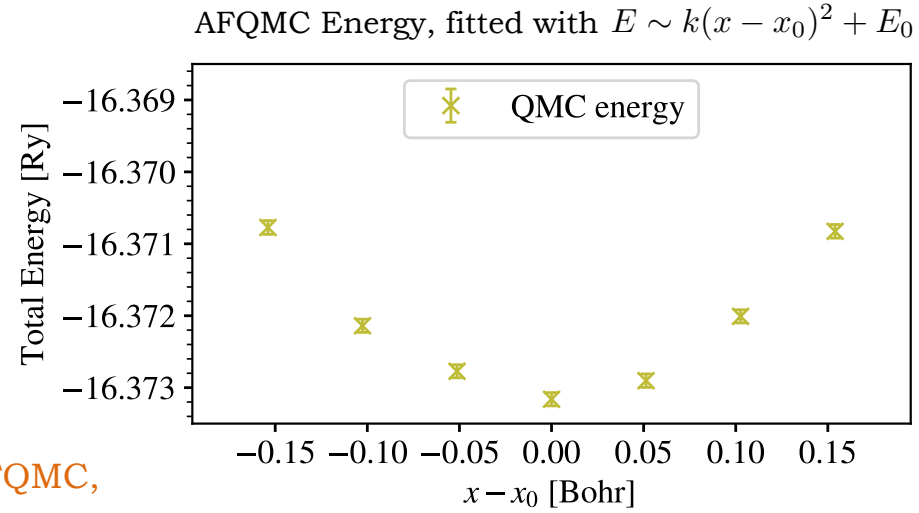
$$-\frac{\partial E_{\text{elec}}}{\partial \vec{\tau}_i} = -\frac{\partial}{\partial \vec{\tau}_i}\langle \Phi_0 | H | \Phi_0 \rangle = \langle \Phi_0 | -\frac{\partial H}{\partial \vec{\tau}_i} | \Phi_0 \rangle$$

Can be explicitly evaluated with AFQMC, with "back-propagation"

- Same low scaling as total energy (× a small prefactor, e.g. 1.2)

- Benchmark with AFQMC energy derivatives:





S. Chen and S. Zhang, *Phys. Rev. B* **107**, 195150 (2023)

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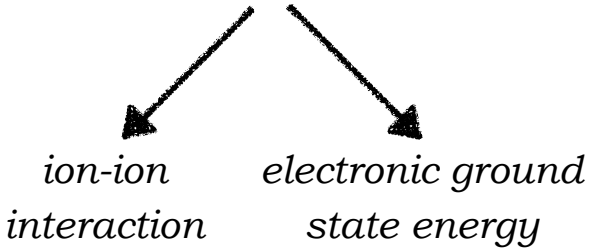

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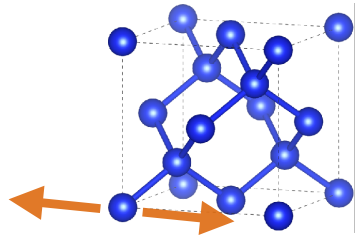

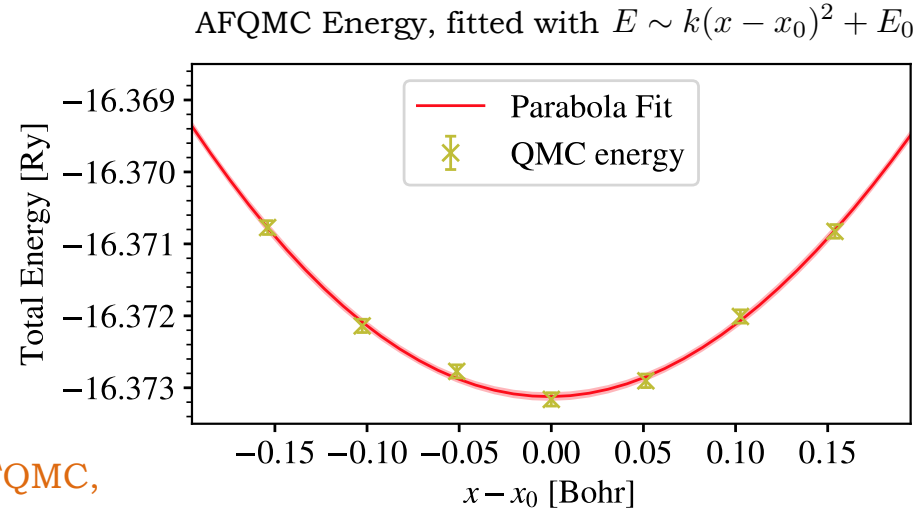

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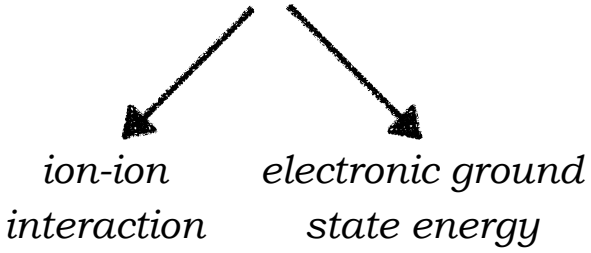

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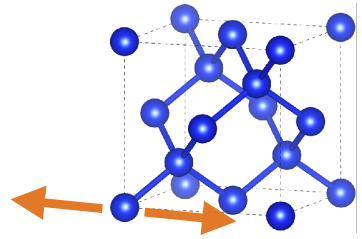
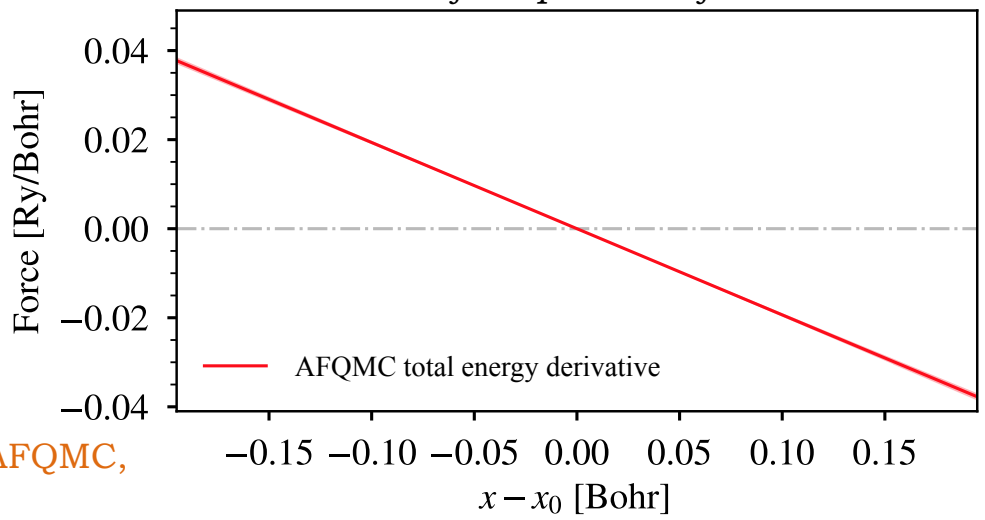


Take derivative of the parabola function:



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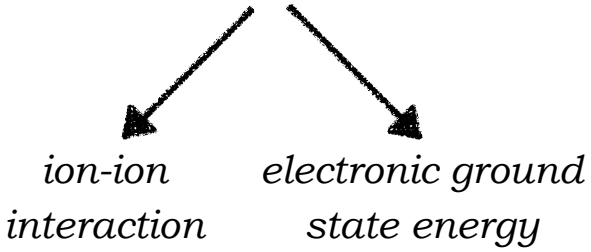

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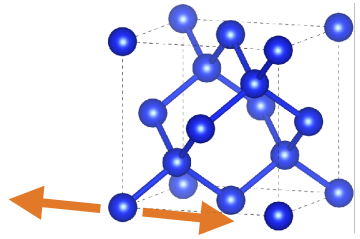
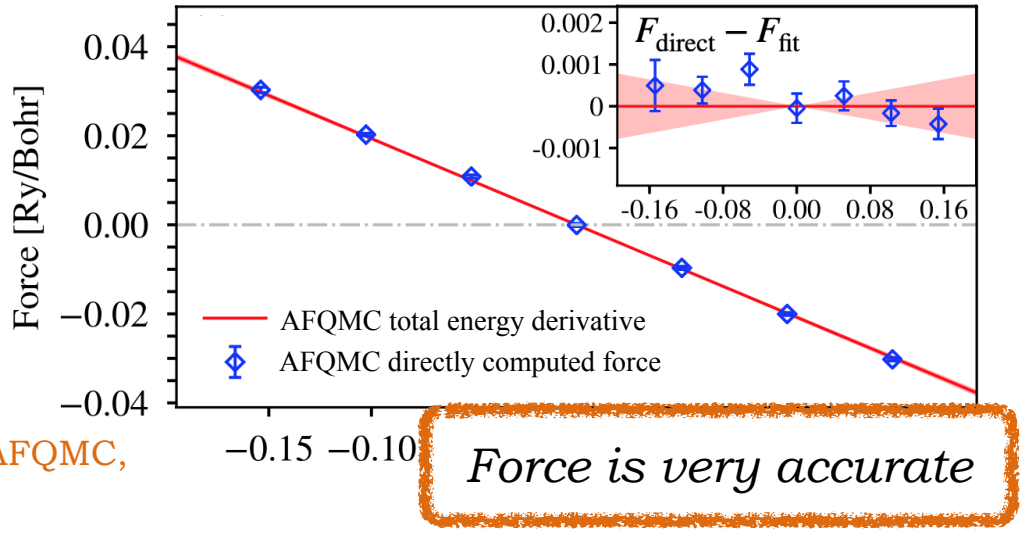


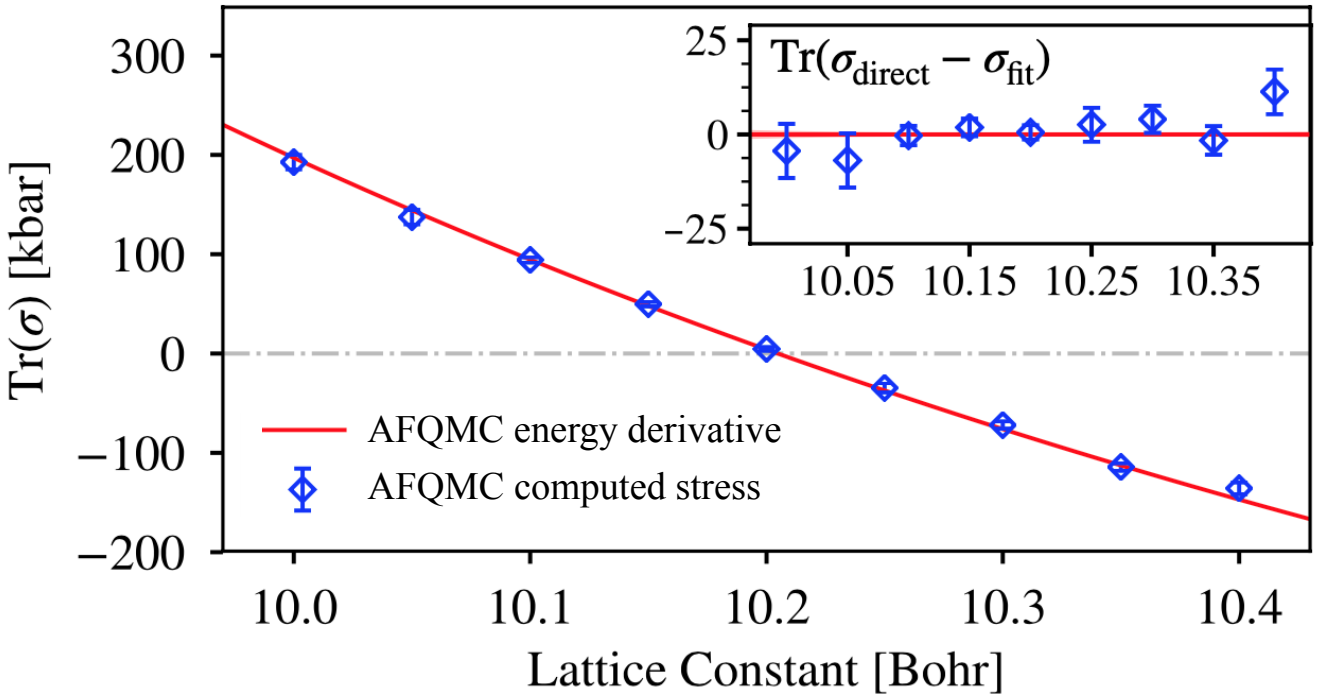


Force is very accurate

S. Chen and S. Zhang, *Phys. Rev. B* **107**, 195150 (2023)

Stresses with AFQMC

- We also computed stress (derivative to cell shape/volume) and benchmarked its correctness



Excellent stress too!

S. Chen and S. Zhang, *Phys. Rev. B* **107**, 195150 (2023)

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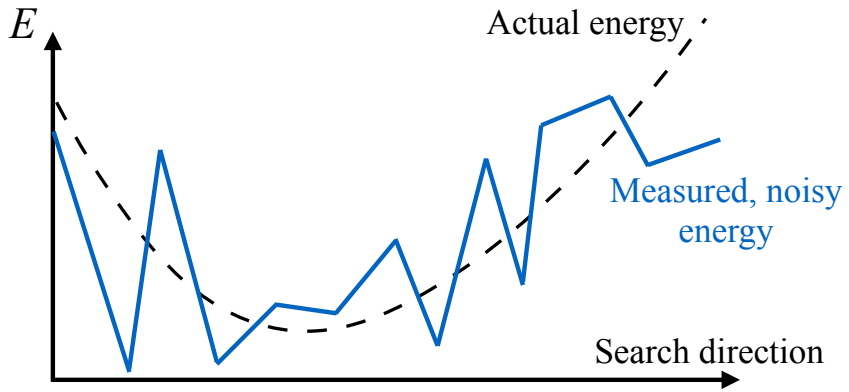
Common optimization algorithms + AFQMC forces?

★ Features of AFQMC forces

- ✦ (relatively) expensive
  - ➡ Scaling is excellent, but prefactor is large vs. DFT
    → we should avoid repeated computations
- ✦ Stochasticity
  - ➡ The actual force magnitude & direction is not known
  - ➡ Error bars are tunable, $\varepsilon \propto C^{-1/2}$
    (allowing large [e.g. >50% × signal] error bars can make calculations ***very*** cheap
    → we **want** such algorithms!)

★ Common algorithms does not interplay well

- ✦ Line search algorithms
  (steepest descent, conjugate gradient, …)
  - ➡ Each line search step = many QMC steps
    → many unused steps, expensive!
  - ➡ With large QMC error bars, minimum-on-line is hard to locate



S. Chen and S. Zhang, *Nat. Comput. Sci.* **2**, 736 (2022)

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★ Common algorithms does not interplay well

- ✦ Newton / quasi-Newton methods
  - ➡ Computing Hessian is not directly possible in AFQMC
  - ➡ Approximate via finite-difference?
    → need many QMC calculations at large N_d

$$H_{ij} \approx \lim_{\Delta x_j \to 0} -\frac{\Delta F_i}{\Delta x_j}$$

  - ➡ Small Δx amplifies QMC noises in H
    After inversion, noise in H^{-1} often overwhelms all signal

S. Chen and S. Zhang, *Nat. Comput. Sci.* **2**, 736 (2022)

New structural optimization algorithm for stochastic forces / stresses (FSSD × SET)

★ Common algorithms: interplay badly with stochastic + relatively expensive AFQMC forces

★ We propose an efficient & robust algorithm (FSSD×SET) for stochastic forces

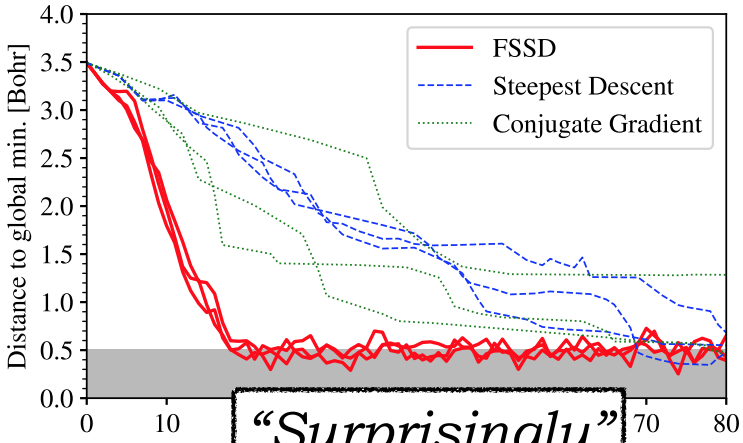
- Update rule: Fixed Step Size Descent

Steepest descent + a few tricks:

① Past force are also used (momentum)

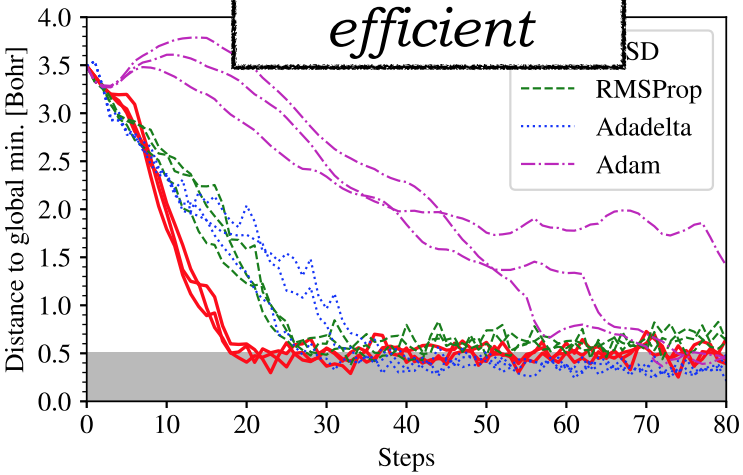
② no line-search to save the time; each move has same length (a initially chosen parameter)

- Convergence speed, vs. 2 line-search algorithms:



"Surprisingly" efficient

- Optimization algorithms also developed in machine learning
- FSSD achieved better efficiency than ML for this problem:



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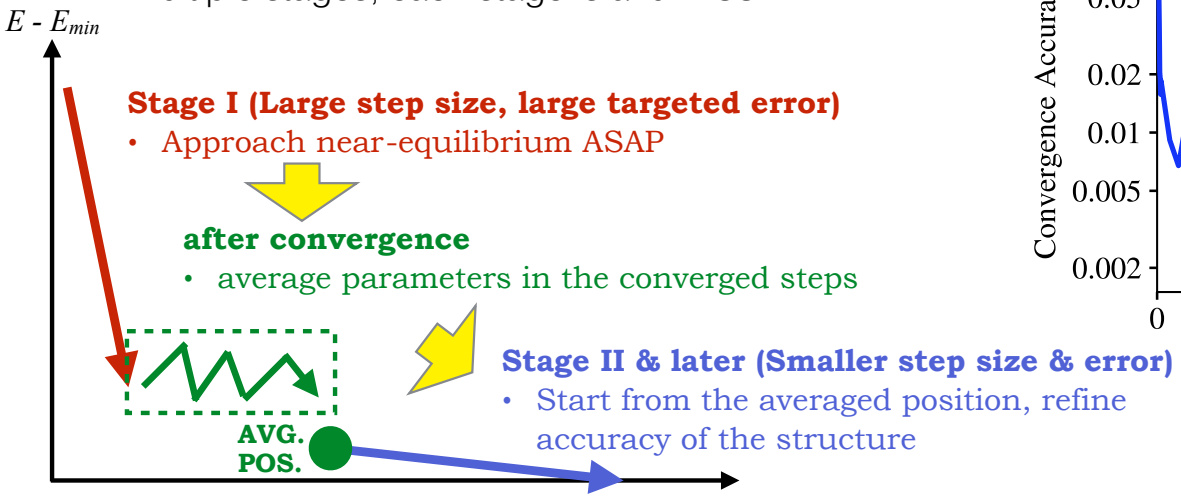
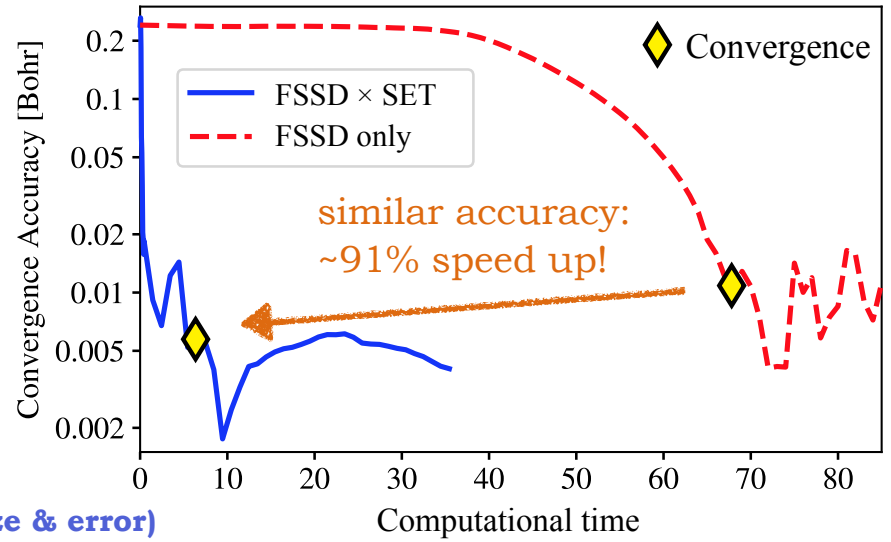
- "Staged Error-Targeting" workflow: multiple stages, each stage is a full FSSD



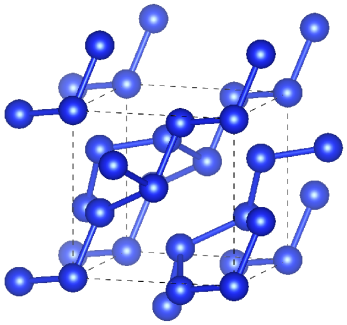
- Improvement with SET:



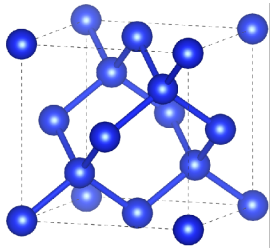
S. Chen and S. Zhang, *Nat. Comput. Sci.* **2**, 736 (2022)

Structural Optimization with AFQMC

- Two examples for full-DOF structural optimizations
- Example 1: Si geometry optimization
  (atom coordinates ***optimizing***, lattice shape/volume ***fixed***)

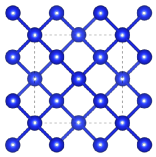


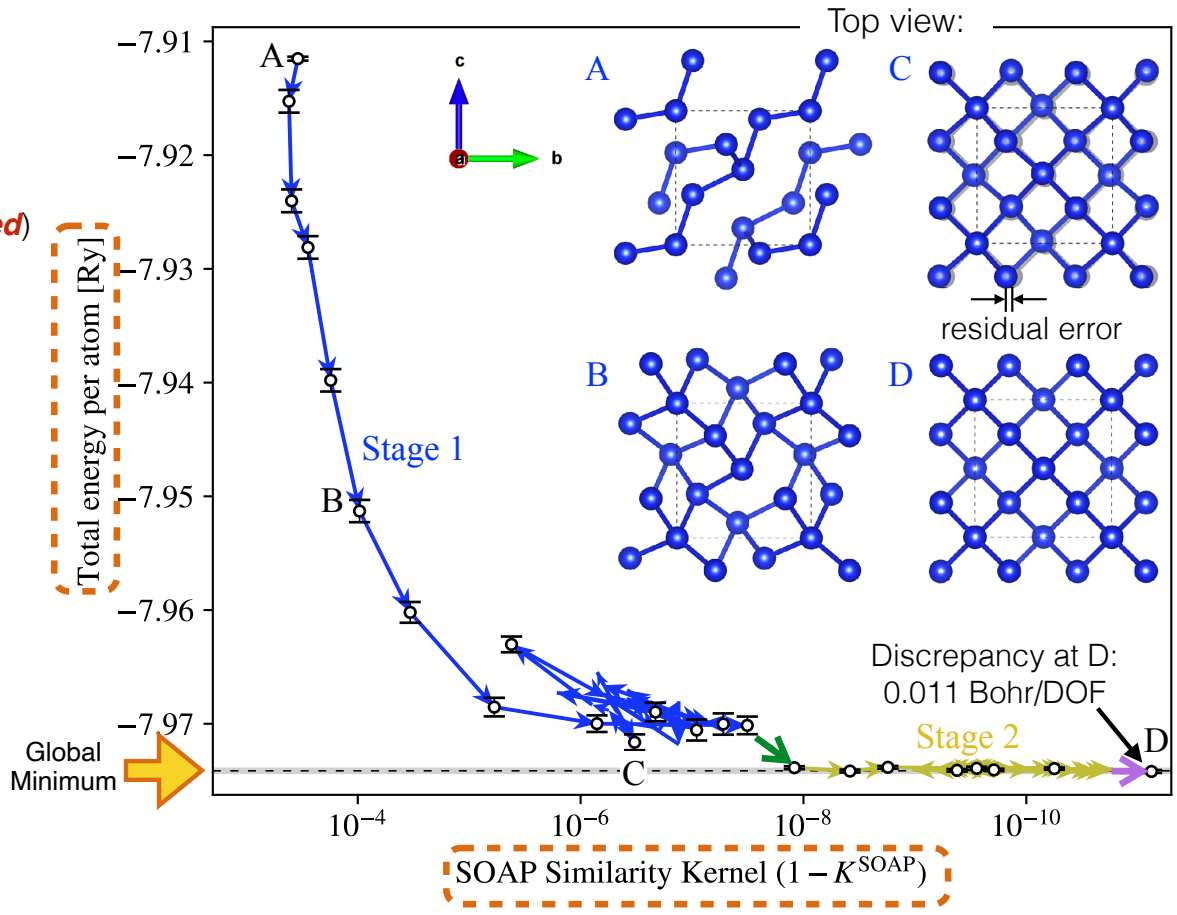
50:50 Mix of two Si phases (Si-I and Si-II)



Diamond structure (global minimum, Si-I)

Top view:

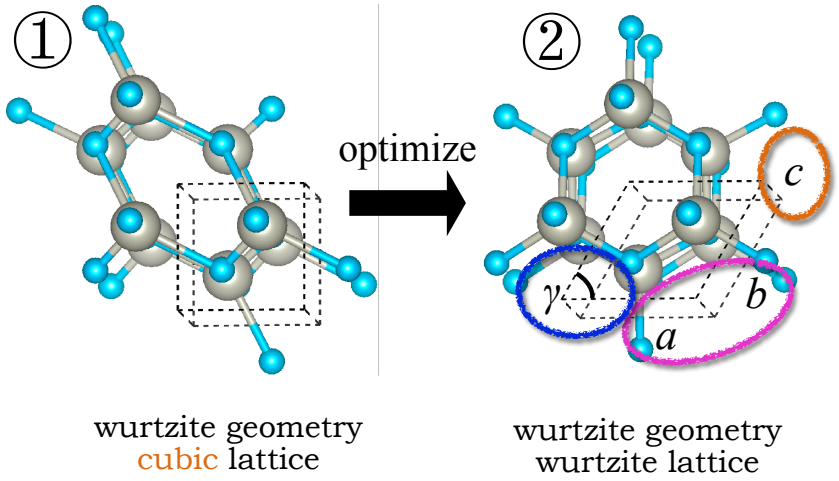


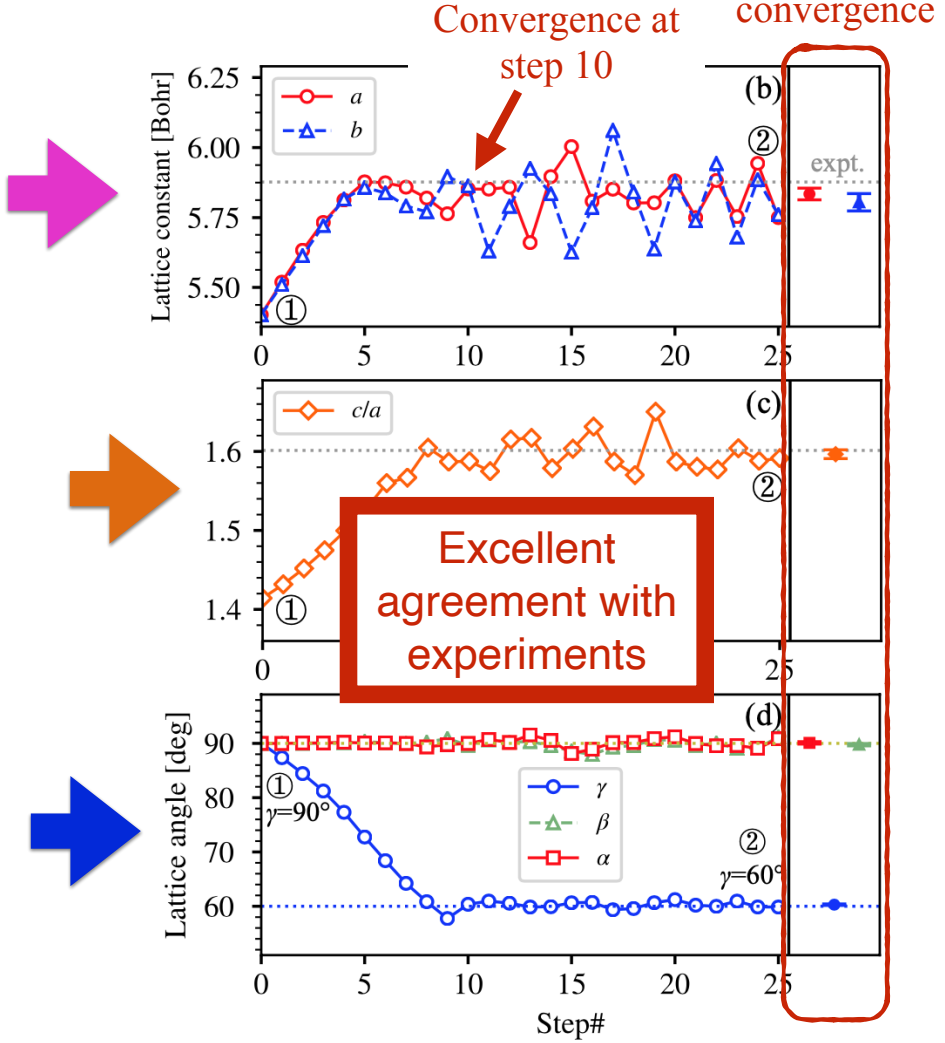


S. Chen and S. Zhang, arXiv: 2302.07460 (submitted to Phys. Rev. B)

Structural Optimization with AFQMC

- Example 2: Find the ground-state cell shape for AlN
  (atom coordinates ***fixed***, lattice shape/volume ***optimizing***)





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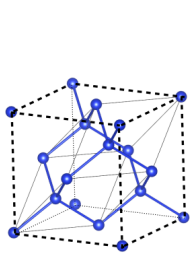
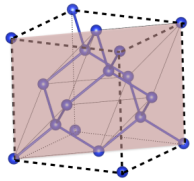
Charge Density

- We computed **charge densities** in several different solids:

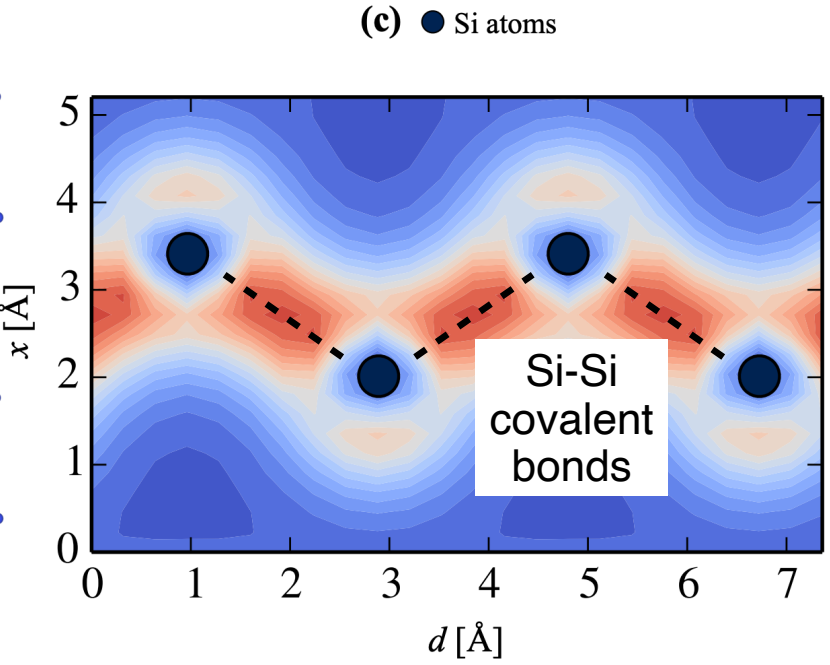
S. Chen, M. Motta, F. Ma, and S. Zhang, *Phys. Rev. B* **103**, 075138 (2021)



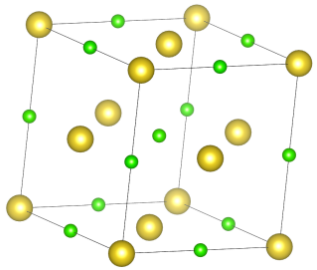
(a)

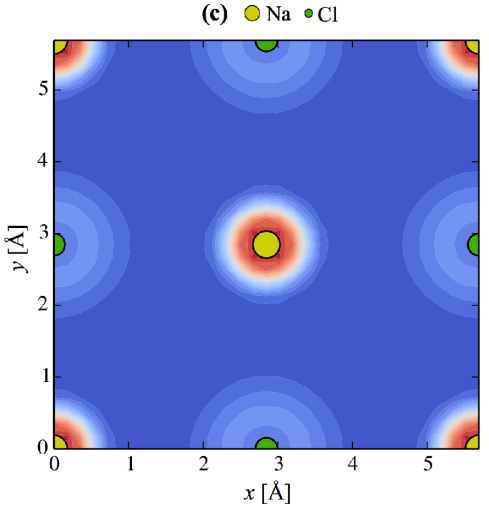


(b)



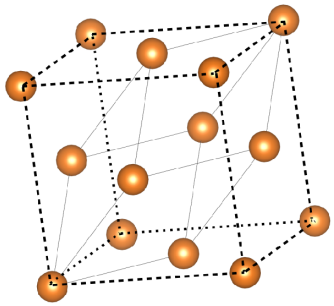
- Ionic crystal NaCl

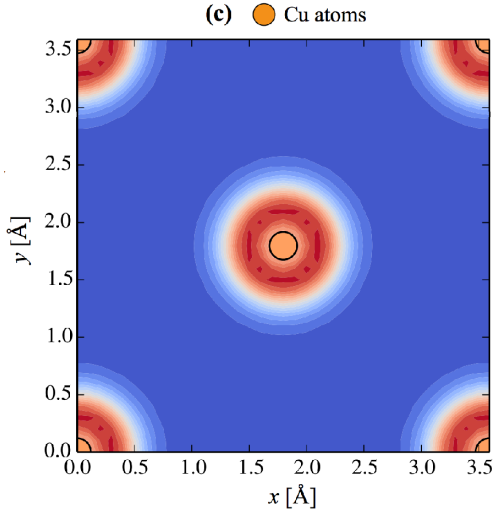




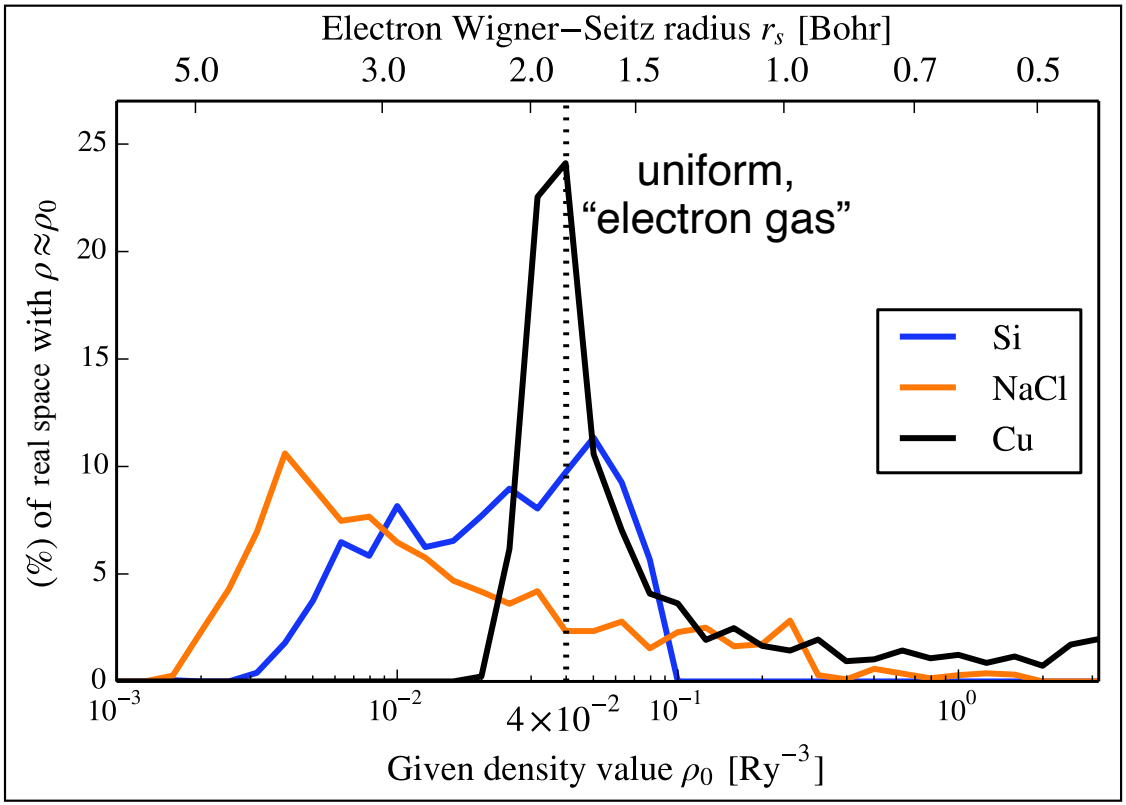
density around ions instead of forming bonds

- Transition metal Cu



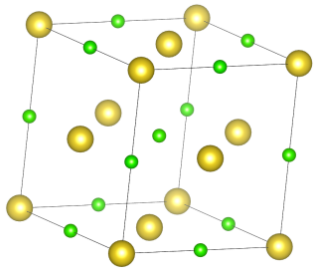


Charge Density

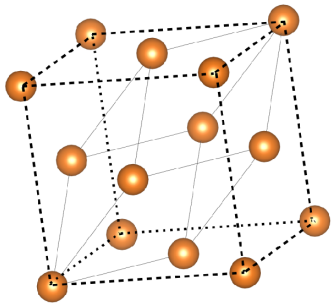


S. Chen, M. Motta, F. Ma, and S. Zhang, *Phys. Rev. B* **103**, 075138 (2021)

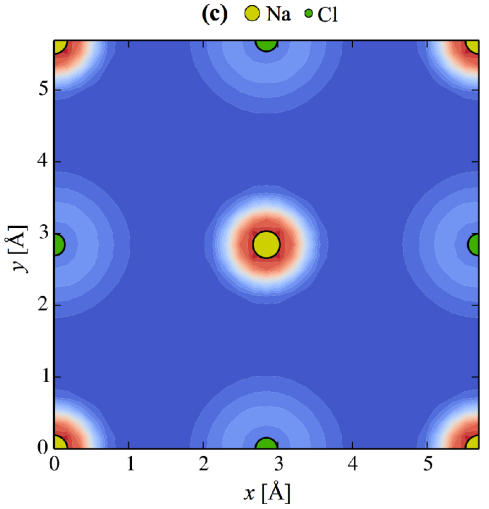
- Ionic crystal NaCl

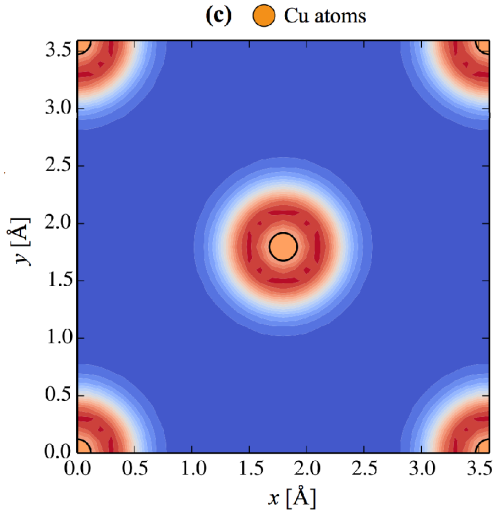


Transition metal Cu



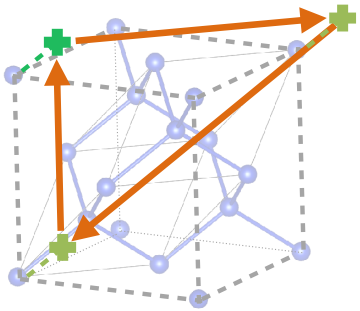
density around ions instead of forming bonds

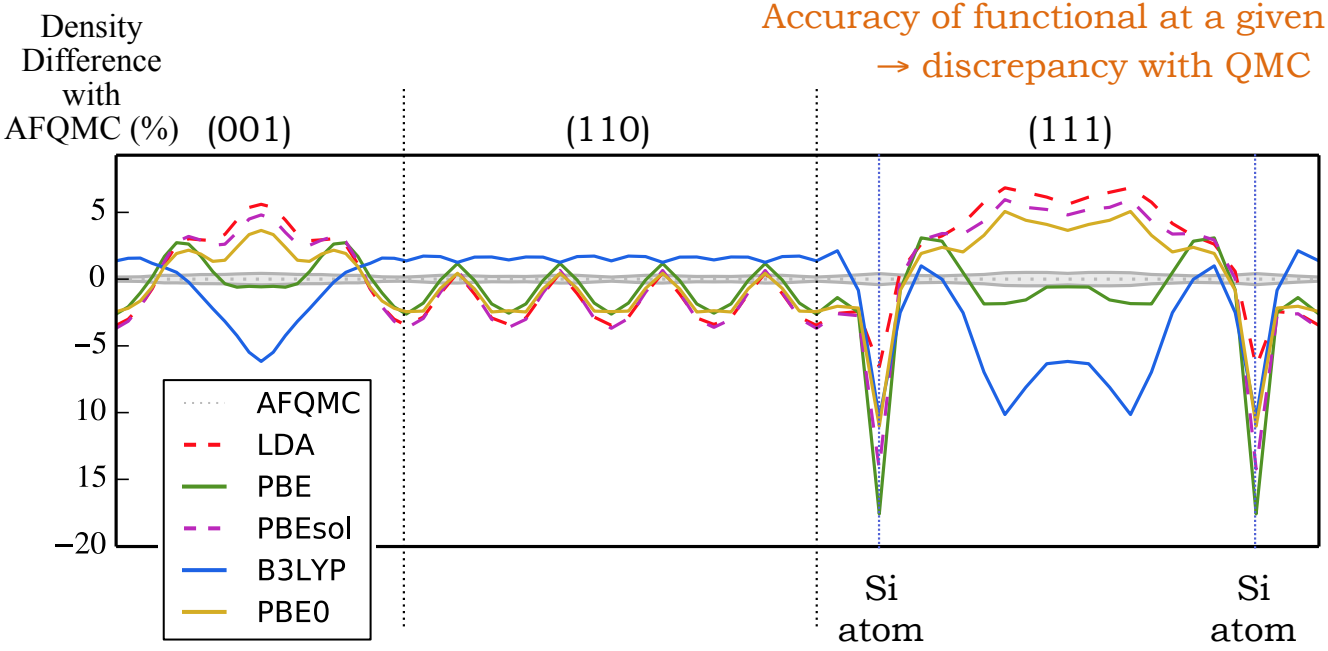




Charge Density

- Benchmarking DFT functionals with our accurate densities:





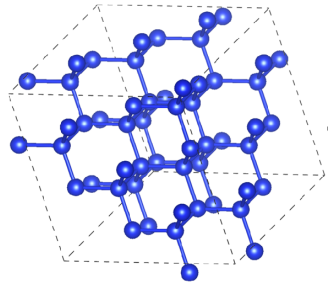
Accuracy of functional at a given point → discrepancy with QMC

S. Chen, M. Motta, F. Ma, and S. Zhang, *Phys. Rev. B* **103**, 075138 (2021)

- Apply AFQMC density to improve DFT functionals →

A. Aouina, M. Gatti, S. Chen, S. Zhang, and L. Reining, *Phys. Rev. B* **107**, 195123 (2023)

Phonon spectrum from AFQMC forces



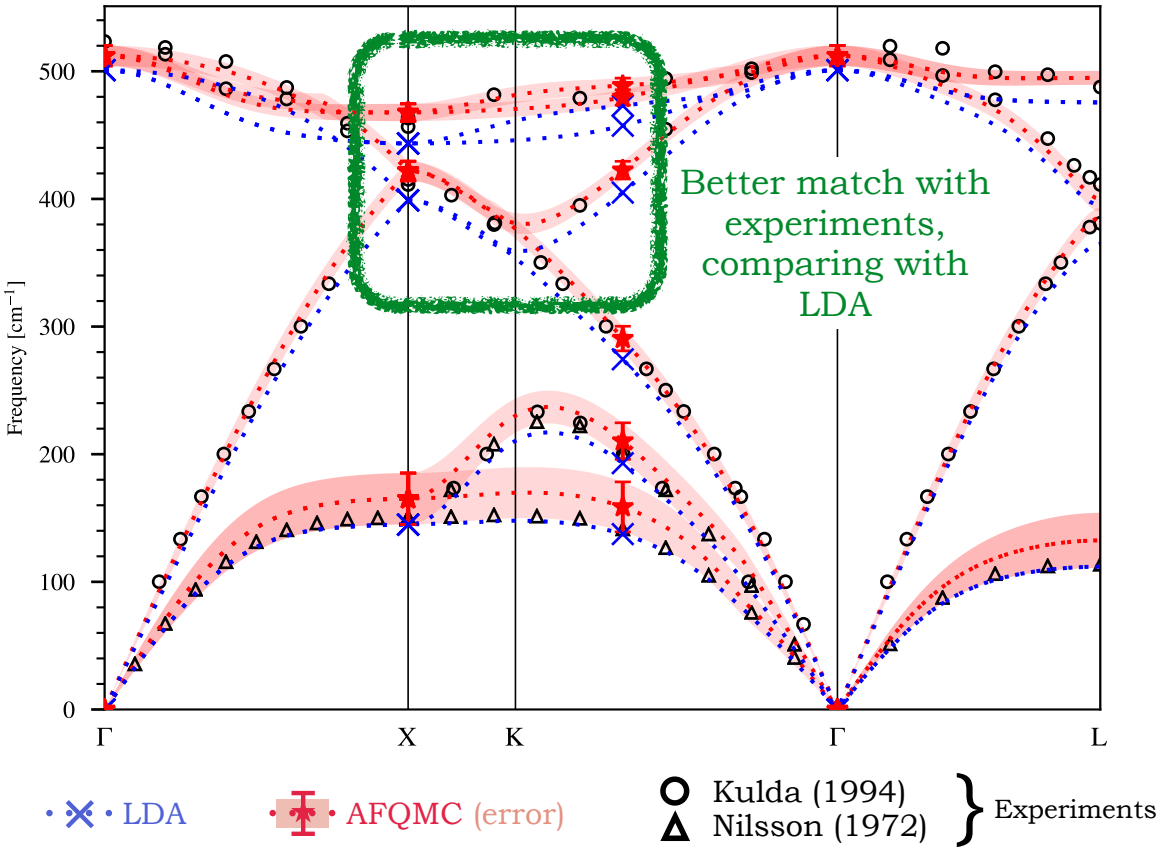
- Frozen phonon method
- We compute accurate and efficient IFCs from AFQMC forces via our new technique of correlated sampling + population control

{ S. Chen*, Y. Yang*, M. A. Morales, and S. Zhang, *to be submitted* }

➡ Thermodynamic properties (U, C_V, S, …)

➡ Study of electron-phonon coupling in superconductors

Result: Si phonon spectrum



S. Chen and S. Zhang, *in preparation*

Summary

- ➡ Forces / stresses are the key to structural predictions
- ➡ Methods beyond DFT (“many-body” methods) are needed for difficult structure problems
- ➡ Many-body forces are usually technically challenging

- In AFQMC, we present *direct* Hellmann-Feynman computation of forces and stresses.
- We propose an algorithm (FSSD×SET) for efficient and robust geometry optimization under stochastic gradients like (but not limited to) QMC forces.
- Accurate & efficient full-DOF structural optimization in solids are now possible for beyond-DFT problems
- Other physical properties of solids have also become approachable with AFQMC: charge density, phonon spectrum, Berry phases, ...

Thank you!