Accurate structural optimizations in solids with auxiliary-field quantum Monte Carlo

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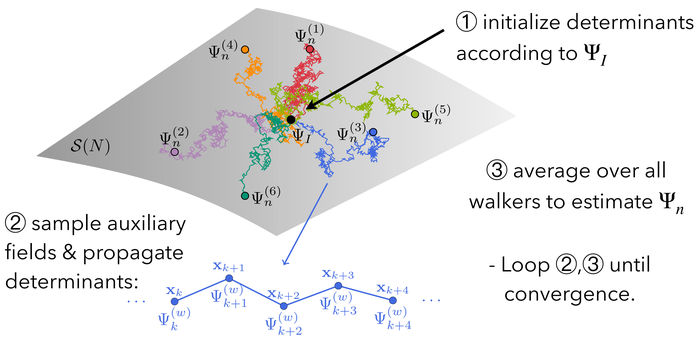
Abstract

Structural optimization by accurate, non-perturbative methods has been an outstanding challenge in many-body electronic structure computations. We present direct computation of forces and stresses in solids by plane-wave AFQMC. With them, we perform full structural optimizations in several solids. Additionally, we propose a general optimization algorithm, FSSD×SET, for gradients which have intrinsic stochastic noise. This algorithm is found to outperform standard optimization methods and several machine learning algorithms in efficiency and robustness.

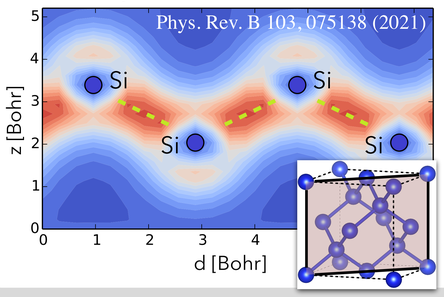
Auxiliary-field QMC

AFQMC [1-3] approaches the ground state of a system with imaginary time propagation $e^{-\beta H}|\Psi_I\rangle \rightarrow |\Psi_{\mathrm{GS}}\rangle$. With the introduction of auxiliary fields, two-body propagations transform into integrals of one-body propagations, and can be sampled with a random walk.

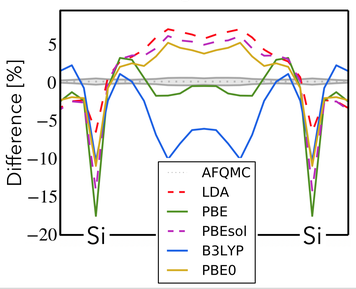


AFQMC has demonstrated excellent accuracy in lattice models, molecules, and solids.

Density of Si (see Ref. [4] for NaCl, Cu)



Benchmarking DFT functionals



Forces and Stresses

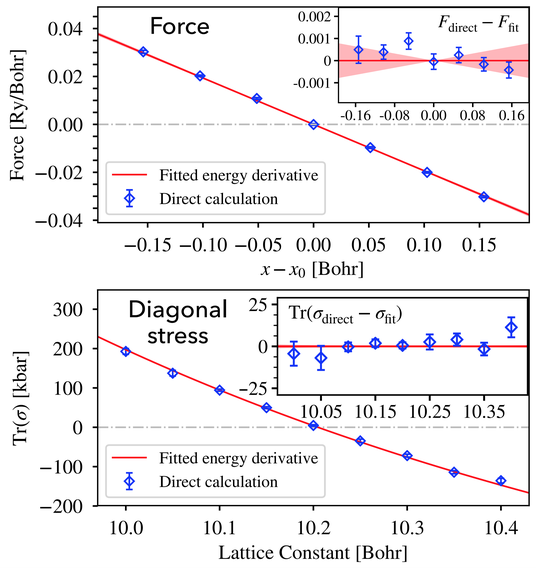
Computation of forces is a kind of "holy grail" in QMC. We present forces and stresses computed directly from BP + Hellmann-Feynman in plane-wave AFQMC [5].

Here we compare:

① directly computed force/stress

② fitting AFQMC equation-of-state and obtaining its derivative

Excellent agreement →



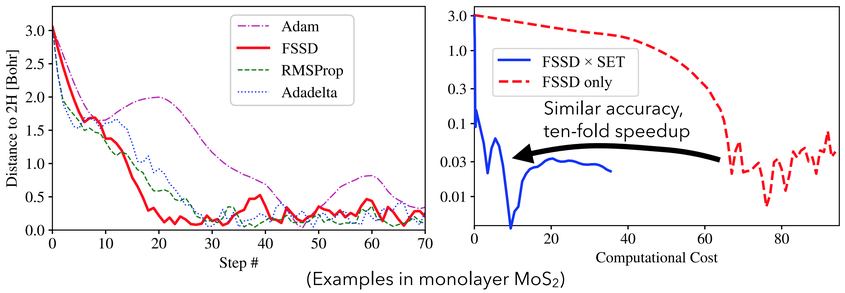
FSSD×SET

AFQMC forces/stresses contain statistical uncertainty. What's the best way to perform structural optimizations in the presence of noisy forces?

We propose a new algorithm called FSSD×SET (*arXiv:2204.12074* [6]):

- **Update rule** "Fixed Step-size Steepest Descent" (FSSD),
- **Scheduling workflow** "Staged error targeting" (SET).

FSSD outperforms several common machine learning algorithms, while SET provides an additional boost.

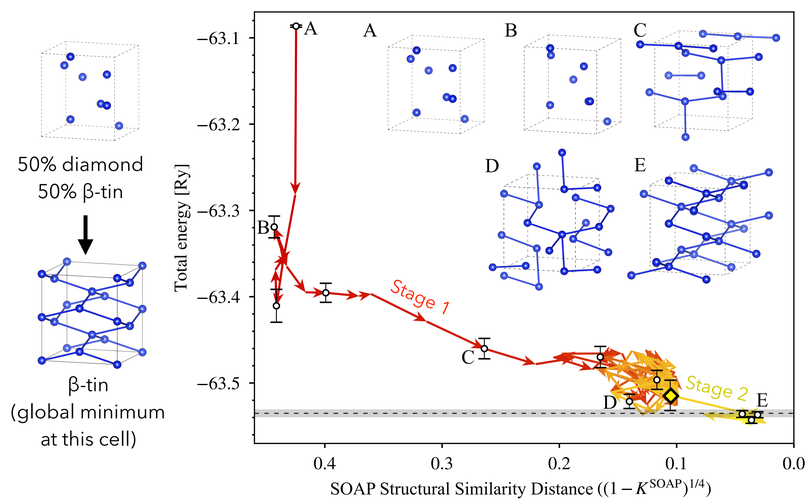


(Examples in monolayer MoS_2)

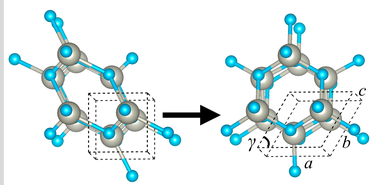
Structural Optimization with AFQMC

With AFQMC forces/stresses and our new optimization algorithm, we perform two direct AFQMC structural optimizations [5].

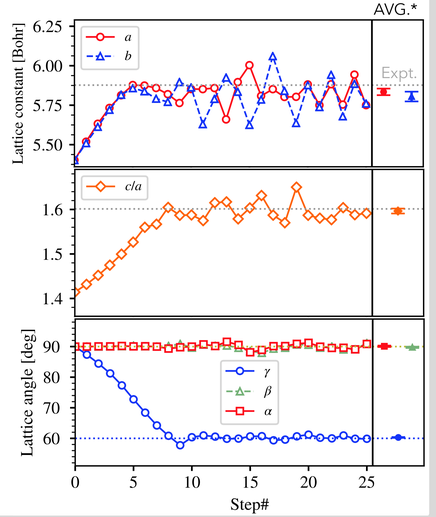
① **Atom-geometry optimization: Si (diamond → β-tin)**



② **Lattice optimization: AlN**



AVG.*



*AVG. = average of lattice parameters after convergence (required by SET)

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2. M. Motta and S. Zhang, *J. Chem. Theory Comput.* 13, 5367 (2017)
3. M. Suewattana, W. Purwanto, S. Zhang, H. Krakauer, and E. J. Walter, *Phys. Rev. B* 75, 245123 (2007);
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5. **S. Chen and S. Zhang, *in preparation;***
6. **S. Chen and S. Zhang, *arXiv:2204.12074* (2022).**

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