

Surrogate Hessian Accelerated DMC Structural Optimization

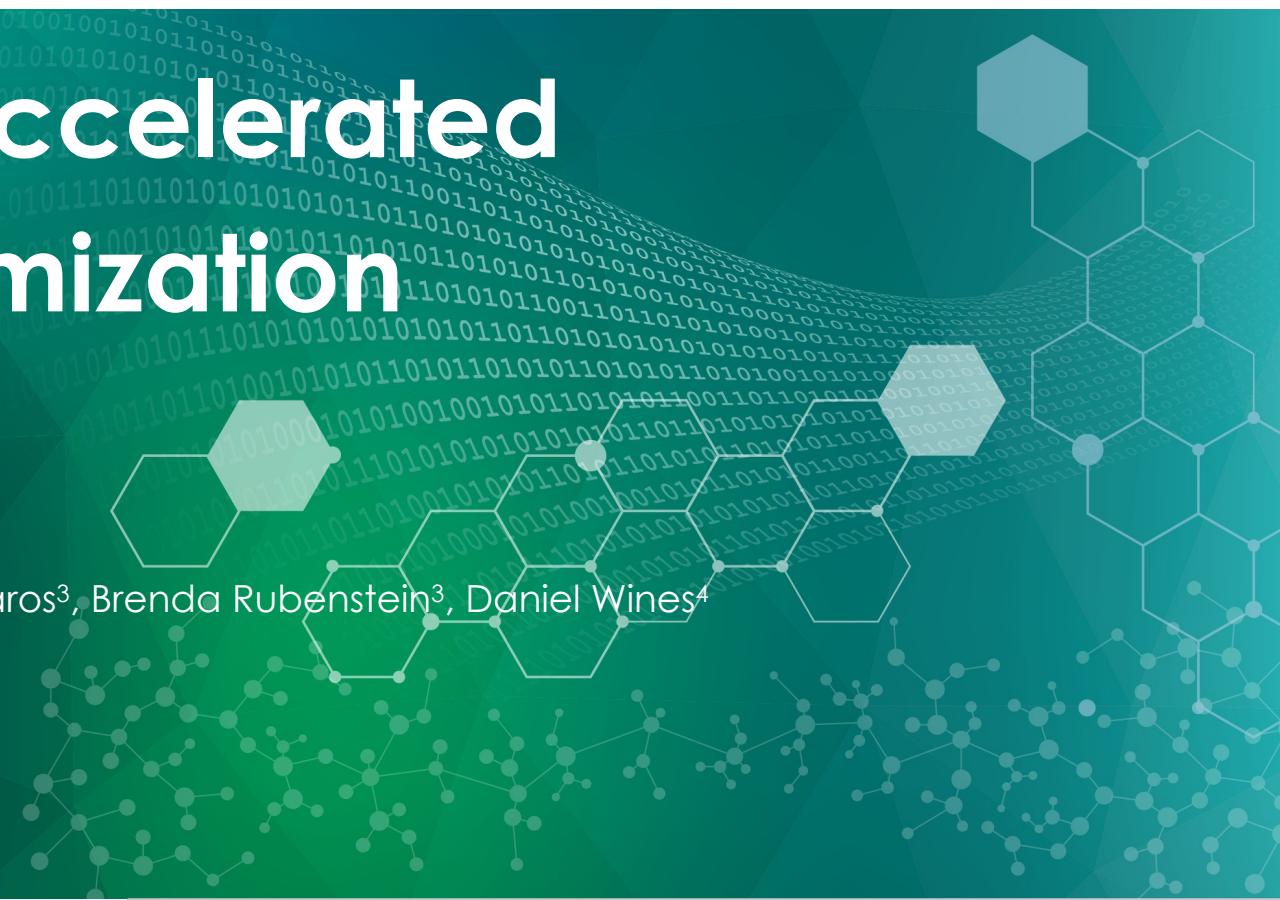
QMCPACK Users Workshop 2023

13 December 2023

Jaron T. Krogel¹, Hyeondeok Shin², Juha Tiilonen¹, Dan Staros³, Brenda Rubenstein³, Daniel Wines⁴

¹ORNL, ²ANL, ³Brown, ⁴NIST

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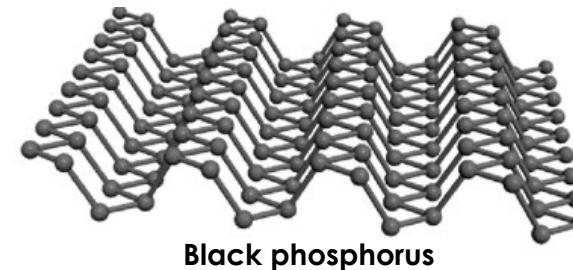


QMCPACK

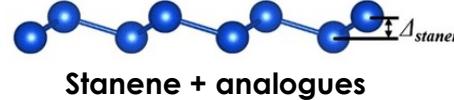
Structure Matters: Quasi-2D Materials

- Quasi-2D materials can show substantial structural sensitivity
- Low energy modes result in large structural variations due to changing chemical environment, or to approximations in theory
- Structural variations couple strongly to optical and magnetic properties
- Accurate theory, such as diffusion Monte Carlo, provide good quality PES
- Major approach: gradient descent methods using statistical forces
- This work: cheap/informative Hessian + mode decomposed energy fitting

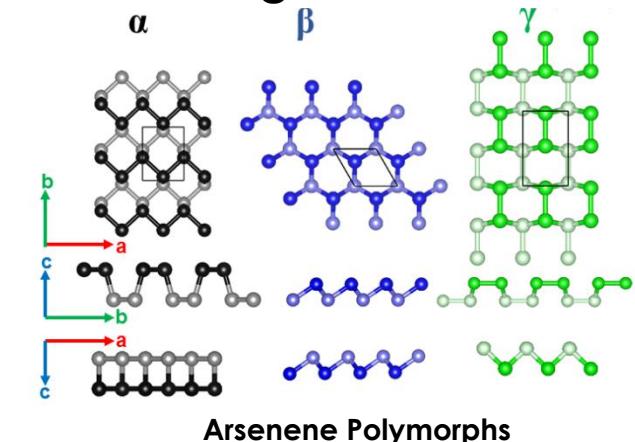
Common phenotype: sensitive corrugation



Perello Nat. Comm. 6 7809 (2015)

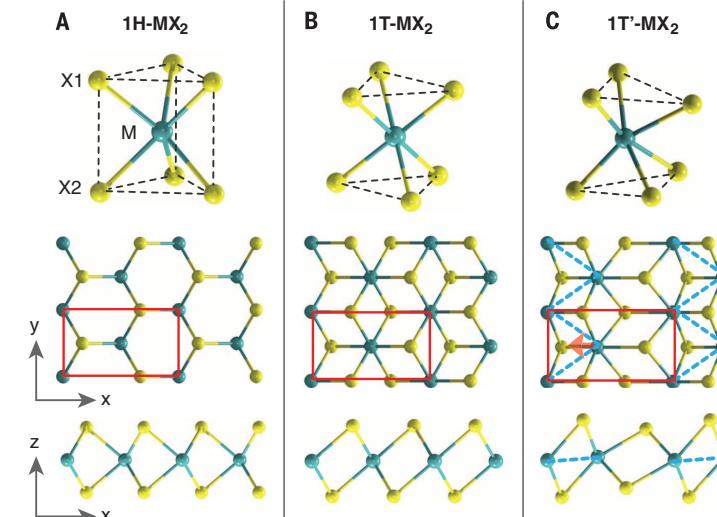


Lu Sci. Rep. 7 3912 (2017)



Jamdagni arXiv 1811 09376 (2018)

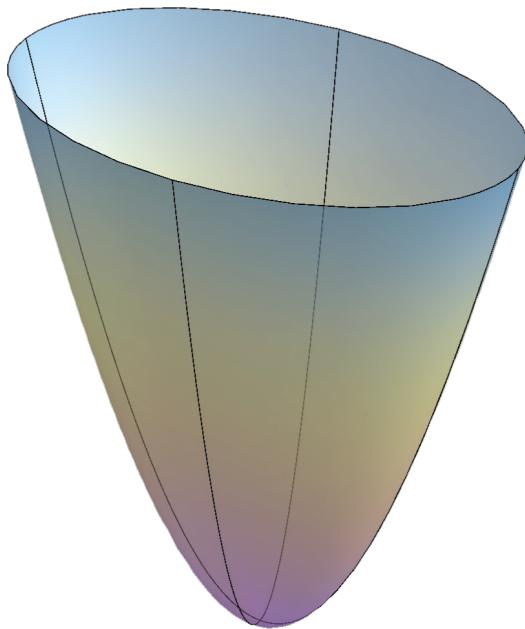
The 1T' distortion in TMD's



Qian Science 346 1344 (2014)

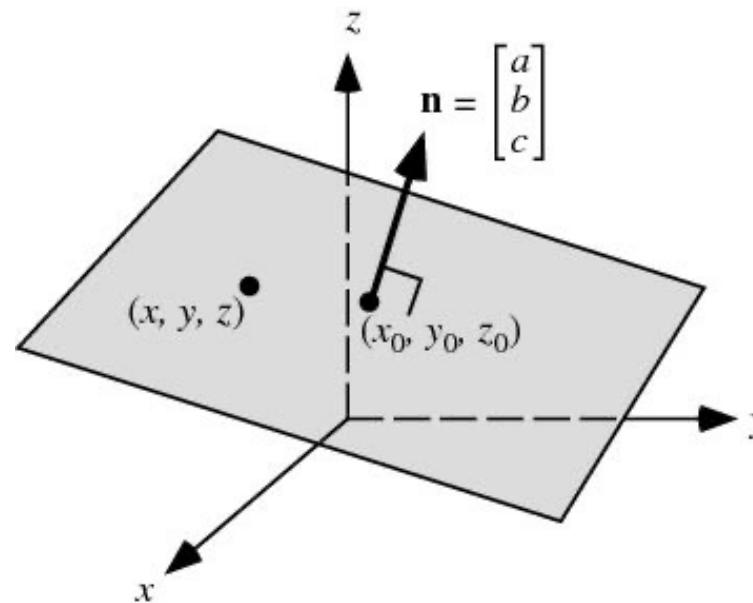
Motivation: Order of Information about Local PES

Energy Hessian



>

Force



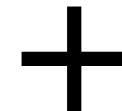
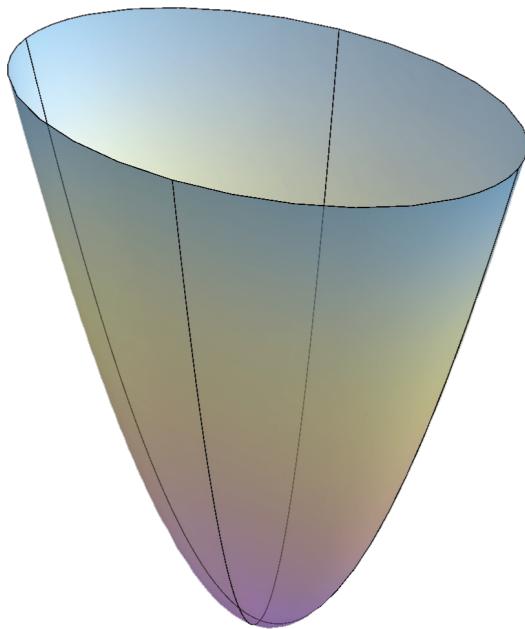
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Energy Value



Motivation: Order of Information about Local PES

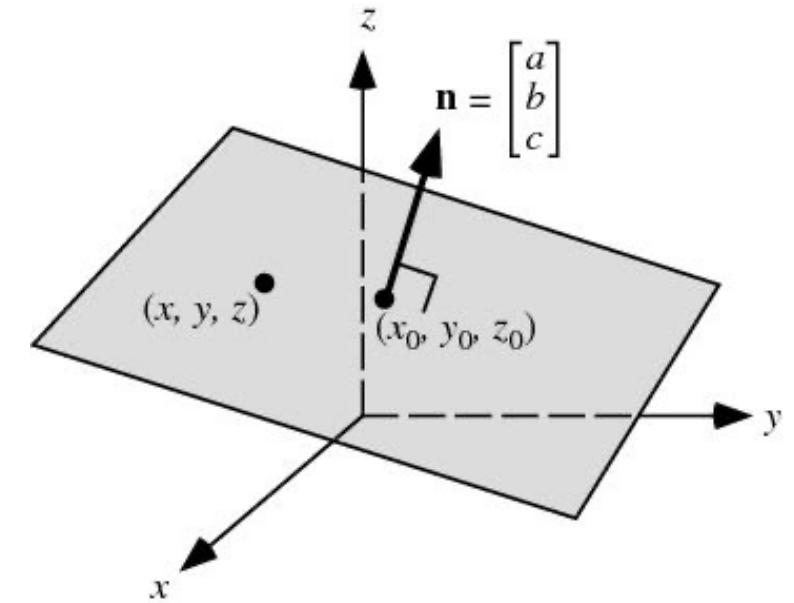
Approximate
Energy Hessian



Exact
Energy
Values



Force

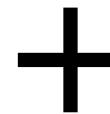
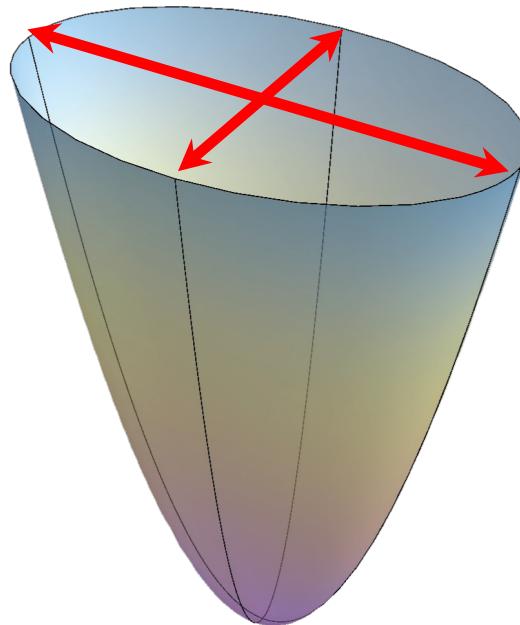


Surrogate Hessian Parallel Line Search Method

Benefits

- Low code: wraps traditional DMC energy evaluation
- Makes efficient use of Hessian information derived from other theories (DFT, MP2, etc)
- Allows for mode adaptation of statistics (soft modes intrinsically cost more than stiff modes)
- Control of systematic and statistical biases
- Accommodates variable cell and atomic structure straightforwardly
- Accommodates any “good enough” trial wavefunction (e.g. DMC with DFT based Slater-Jastrow trial wavefunction for materials w/ transition metals)

**Surrogate DFT
Energy Hessian**



**DMC
Energy**



Surrogate Hessian Parallel Line Search Method

Decoupled d.o.f. via Hessian

$$\begin{aligned} E &= E_0 + \frac{1}{2}(p - p_0)^T H_p(p - p_0) \quad \leftarrow \sim M^2 \text{ energies} \\ &= E_0 + \frac{1}{2}(p - p_0)^T U^T K U(p - p_0) \\ &= E_0 + \frac{1}{2}x^T K x \\ &= E_0 + \frac{1}{2} \sum_{m=1}^M k_m x_m^2 \quad \leftarrow \sim 6M \text{ energies} \end{aligned}$$

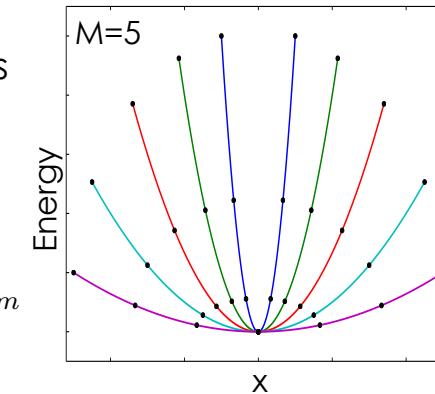
Search Directions

Conjugate Directions

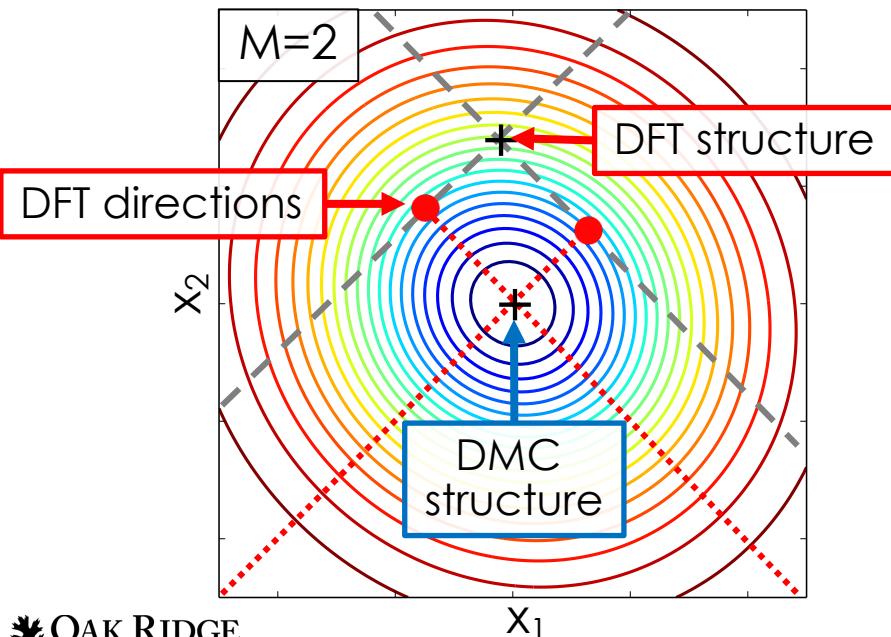
$$d_m = U_m^T$$

Structural Params

$$p(x) = p_0 + \sum_{m=1}^M d_m x_m$$



Parallel Line Search



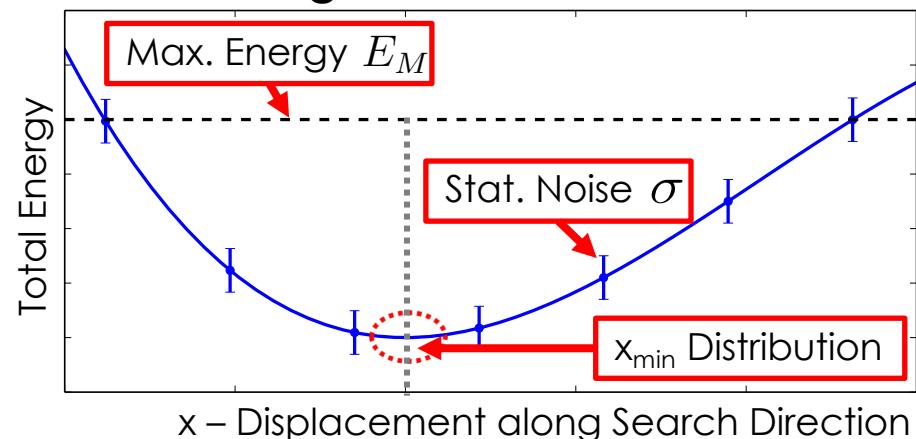
- Method is in family of conjugate direction methods^{1,2}
- Converges in single iteration w/ quadratic PES + perfect directions
- Surrogate DFT structure near quadratic PES regime for DMC
- Surrogate DFT Hessian gives good search directions
(reconstructed from dynamical matrix, finite diff. of stress tensor)
- Final advantage: use DFT PES ($\sim k_m$) to control statistical error/cost

[1] M. J. D. Powell, The Computer Journal **5**, 147 (1962)

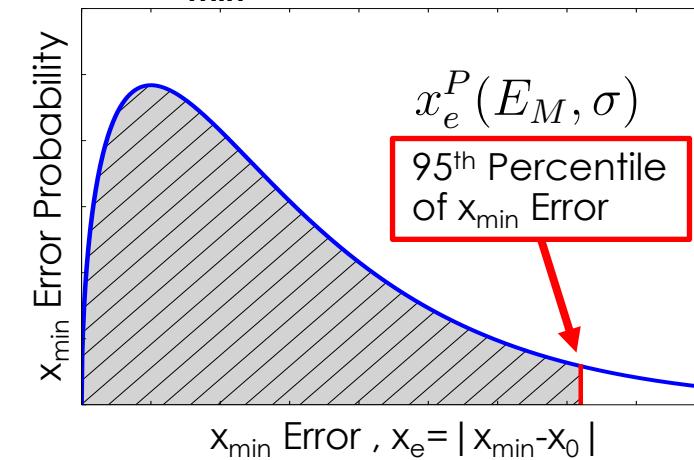
[2] L. K. Wagner & J. C. Grossman, Phys. Rev. Lett. **104**, 210201 (2010)

Surrogacy: Controlling Error while Maximizing Efficiency

Fit to Surrogate PES w/ Added Noise



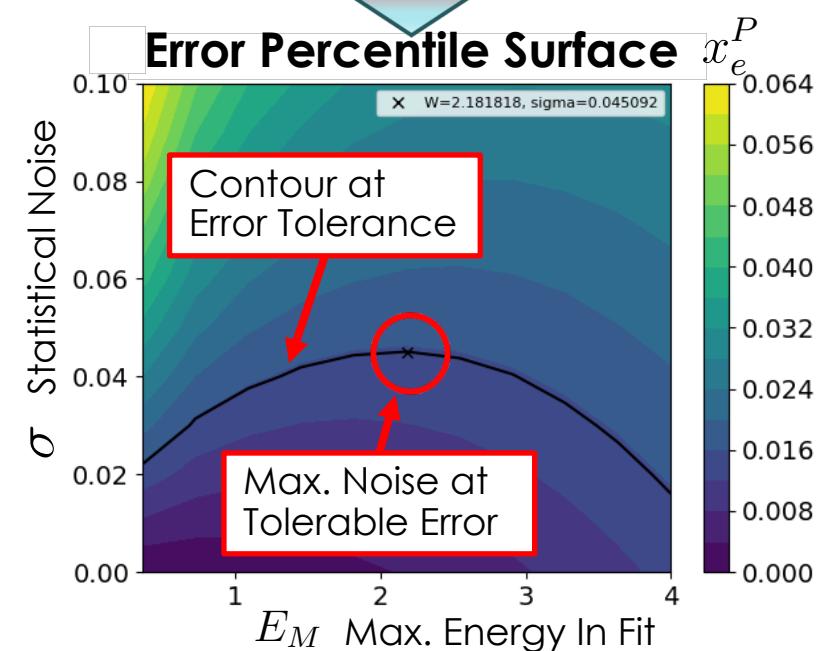
x_{\min} Error Distribution



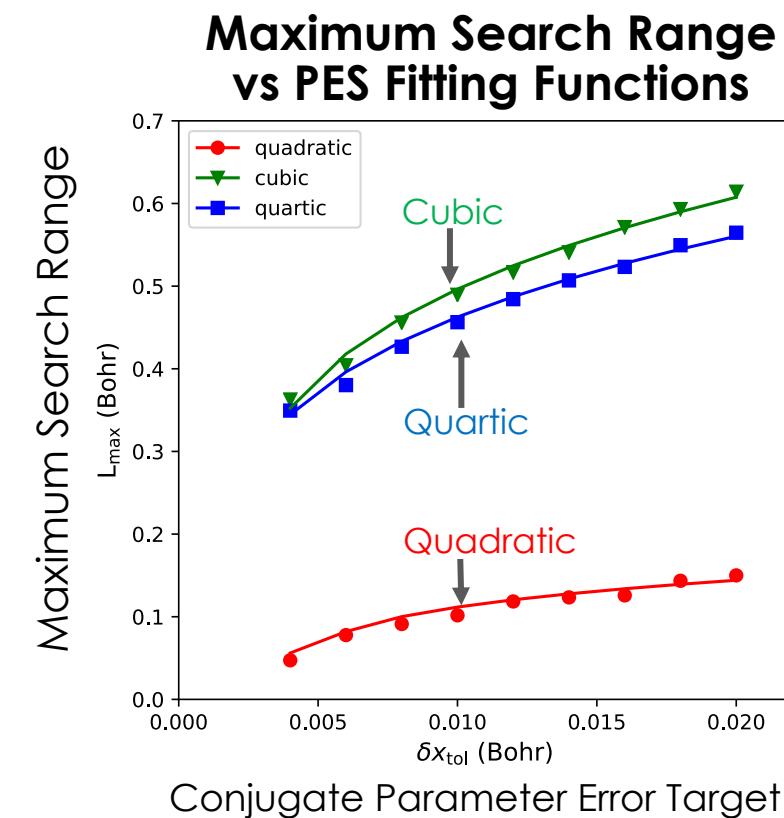
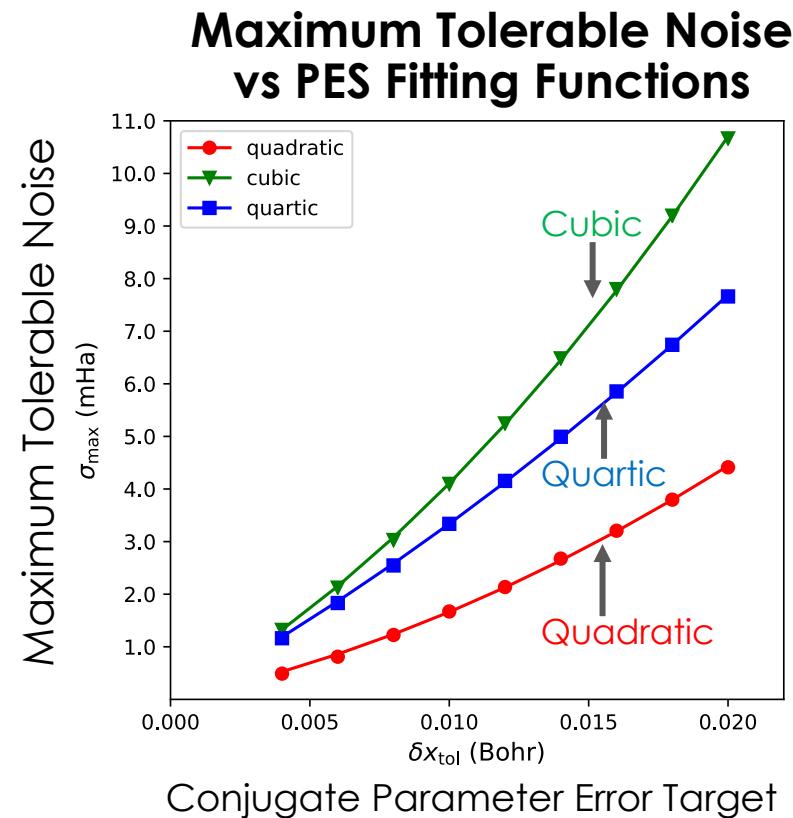
Task: for given tolerable error, find fitting curve allowing maximum noise

- Process gives most efficient DMC noise within target error (systematic + statistical error)
- Noise for each search direction optimized independently
- Complication: errors on search directions mix parameter error non-linearly (requires solution of auxiliary M-dim. optimization problem)

Error Percentile Surface x_e^P

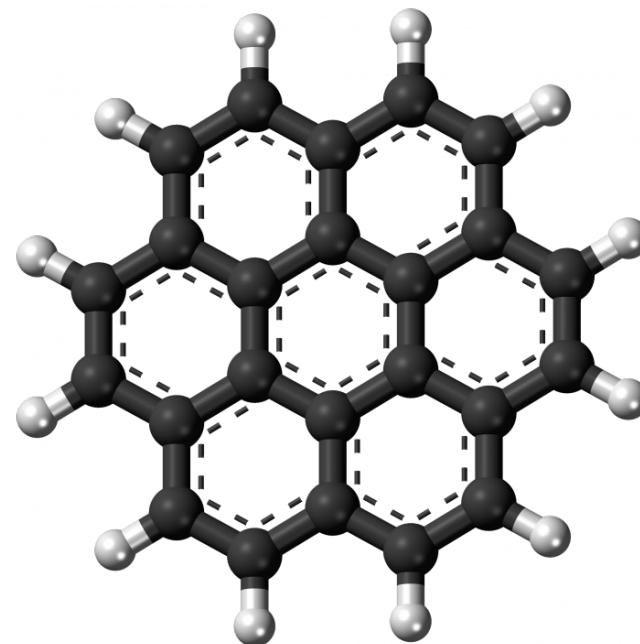


Surrogacy: Controlling Error while Maximizing Efficiency II



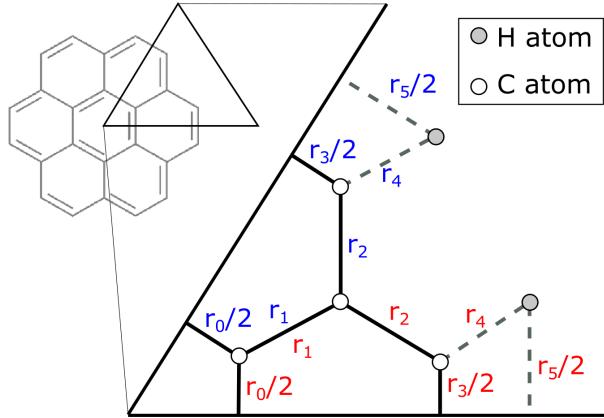
- Tolerable noise maximization algorithm can be used to select optimal PES fitting functions
- Natural options for PES near minimum: low order polynomials (2nd, 3rd, 4th order considered)
- Outcome: Cubic polynomial fits offer highest tolerable noise (up to 7x/2x efficiency gains over **quadratic/quartic**) and largest search range simultaneously

Demonstration in Flake-like Molecules

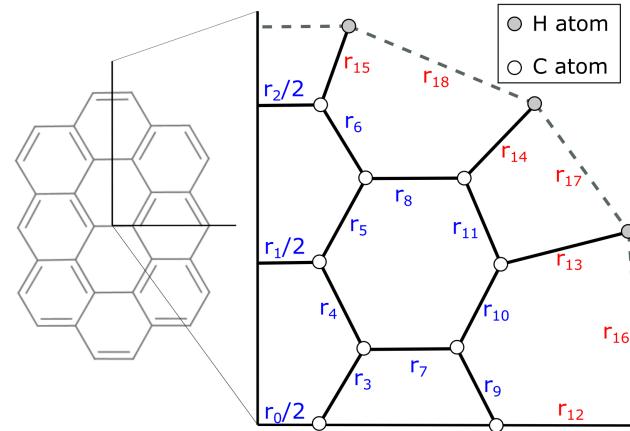


Parameter Couplings in Coronene and Ovalene

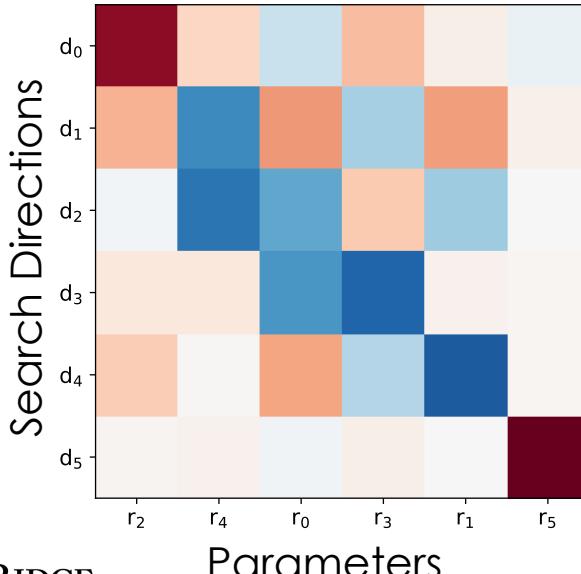
Coronene Parameters



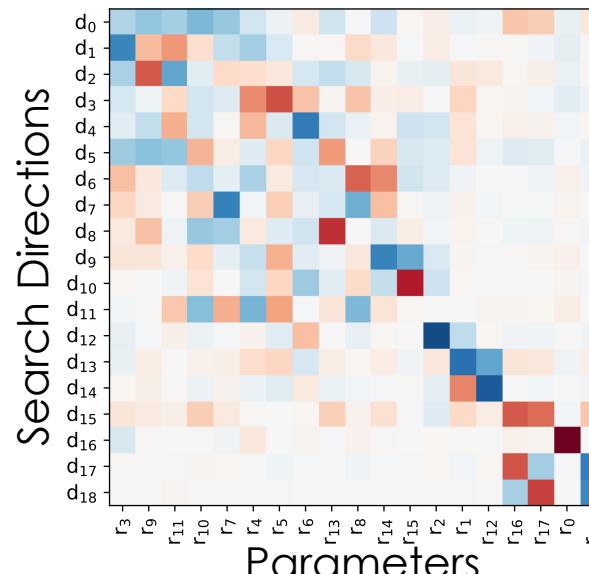
Ovalene Parameters



Coronene Coupling



Ovalene Coupling



Structural Models

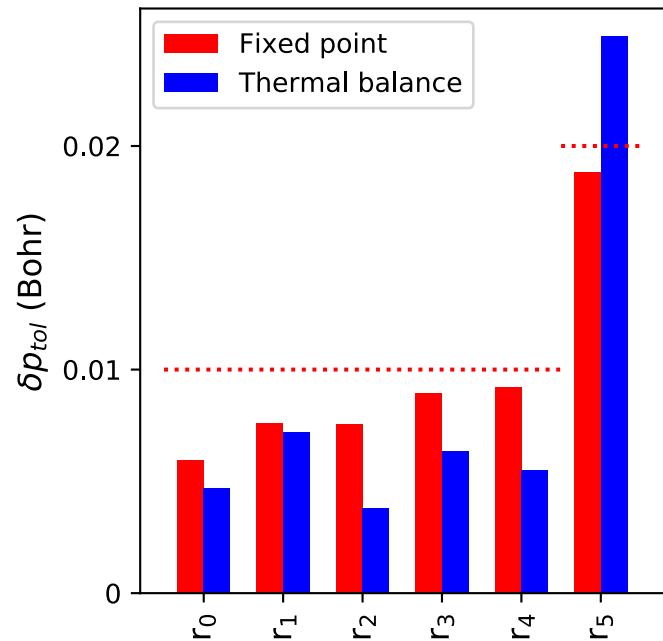
- Bond parameterization
- Coronene: 6 params
- Ovalene: 19 params
- Ovalene harder: larger size and symmetry loss

Coupling Between Parameters

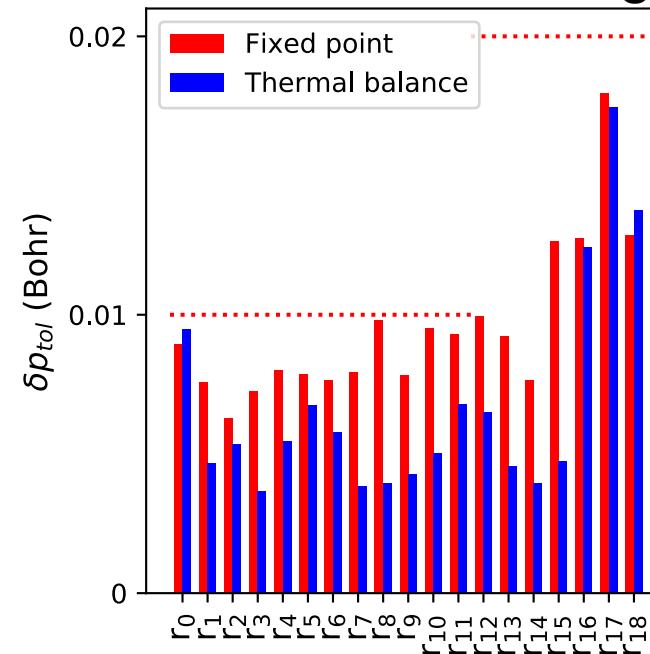
- Strong coupling between C-C bonds
- Moderate coupling between C-H and C-C bonds
- H-H bonds couple with each other, but not with C-C/C-H
- Modes from coupled params give optimal search directions

Surrogacy: Explicit Control of Parameter Errors

Coronene Parameter Targets



Ovalene Parameter Targets



- Systematic and statistical errors from conjugate direction searches mix together into parameter errors
- Need algorithms to minimize cost while meeting separate parameter targets
- Two methods: direct minimization (approx. fixed point) and thermal balancing

Parameter Tolerance and Mapping

$$|\delta p| \leq \delta p_{tol} \quad \delta p = \mathcal{M}(\delta x)$$

Constrained Cost Minimization

$$\delta x_{tol} = \arg \min_{\delta x} \mathcal{C}(\delta x), \quad |\mathcal{M}(\delta x)| \leq \delta p_{tol}$$

$$\mathcal{C}(\delta x) = \sum_{i=1}^N \frac{1}{\sigma_{max}^2(\delta x_i)}$$

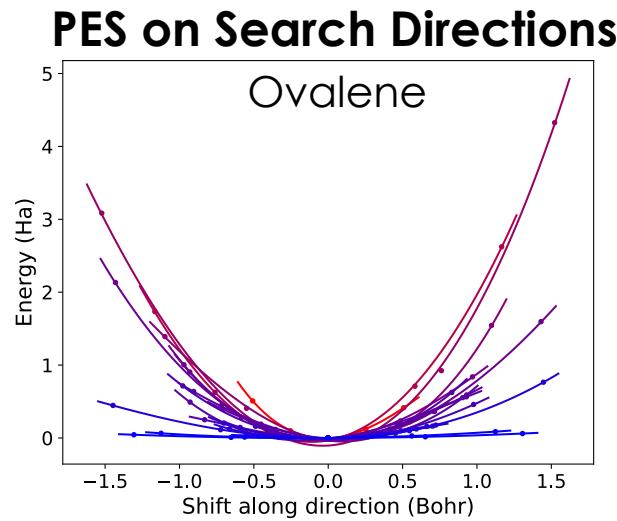
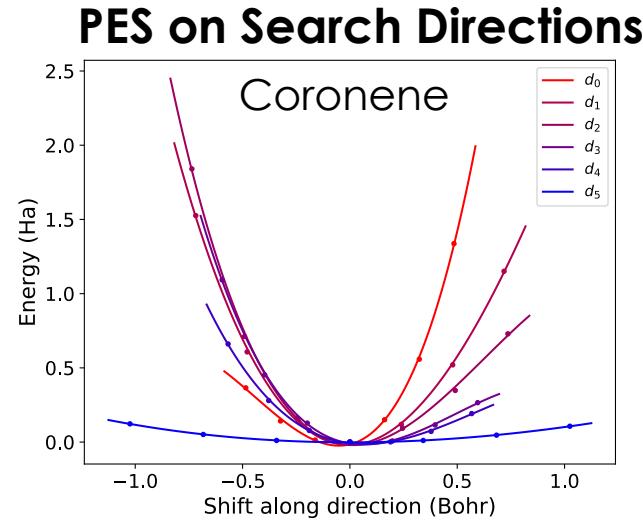
Approximate Fixed Point Inversion

$$\delta x(a, z) = a |z D^T \delta p_{tol} + (1 - |z|) D |^T \delta p_{tol}|$$

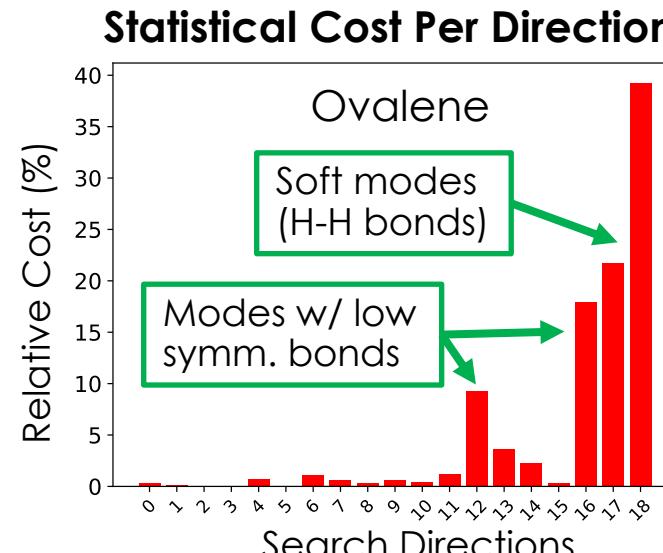
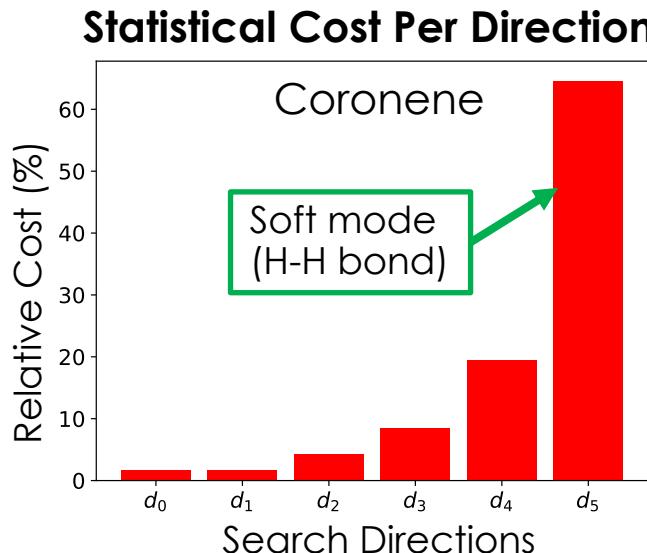
Thermal Balancing of Mode Tolerances

$$\delta x_{tol,n}(T) = \sqrt{\frac{T}{\lambda_n}}$$

Surrogate PES Characteristics and Cost Minimization



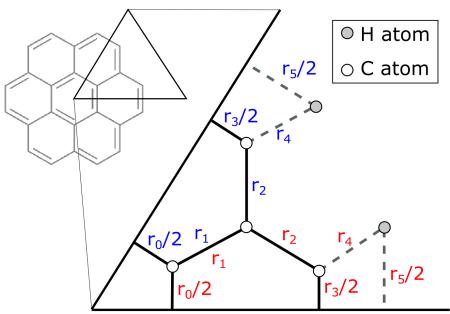
- Curves shown map to a single iteration of line search
- Search lengths set automatically by accuracy constraints
- Naïve cost scales w/ # directions
- But, large spread in stiffness gives opportunity for large savings in statistical costs



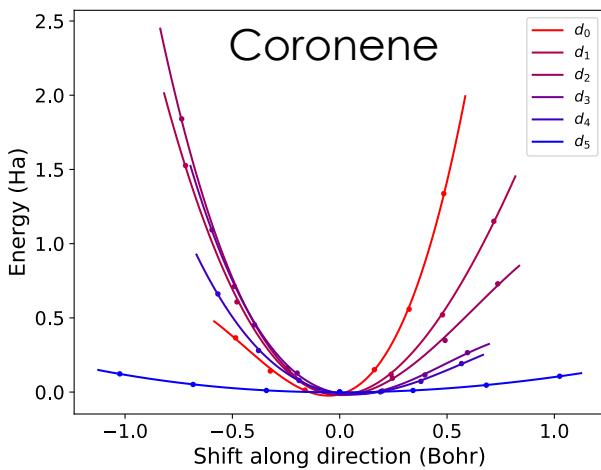
- Tailored statistics, controlled for bias, leads to low costs for many directions
- Remaining costs dominated by modes w/ low stiffness or low symmetry component bonds

Surrogate PES Characteristics and Cost Minimization

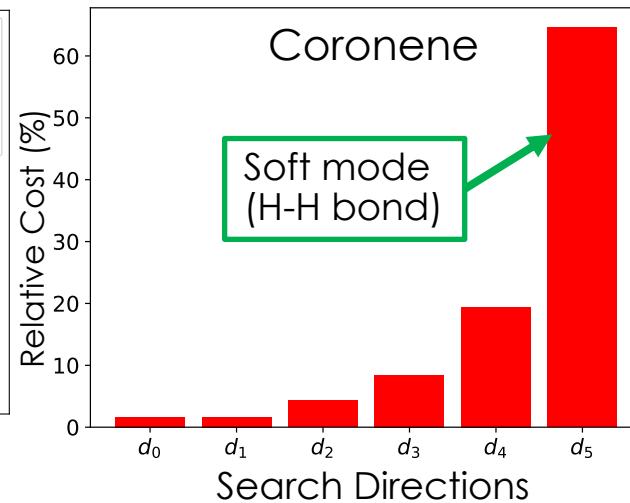
Coronene Parameters



PES on Search Directions

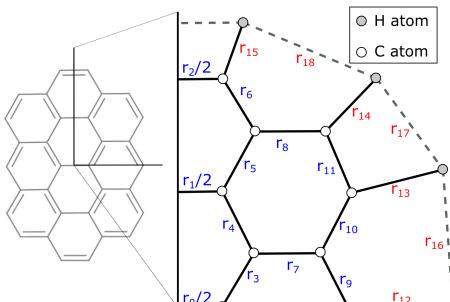


Statistical Cost Per Direction

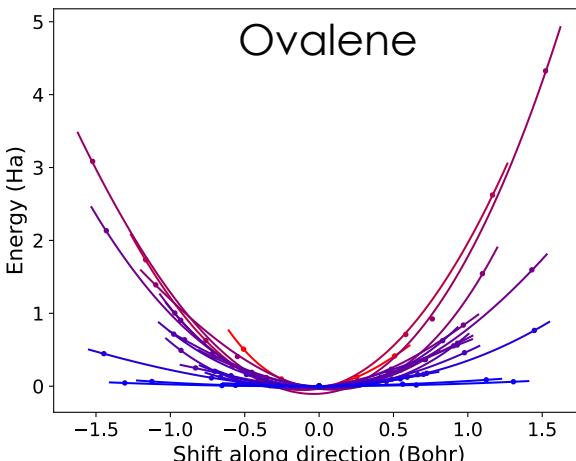


- Curves shown map to a single iteration of line search
- Search lengths set automatically by accuracy constraints
- Naïve cost scales w/ # directions
- But, large spread in stiffness gives opportunity for large savings in statistical costs

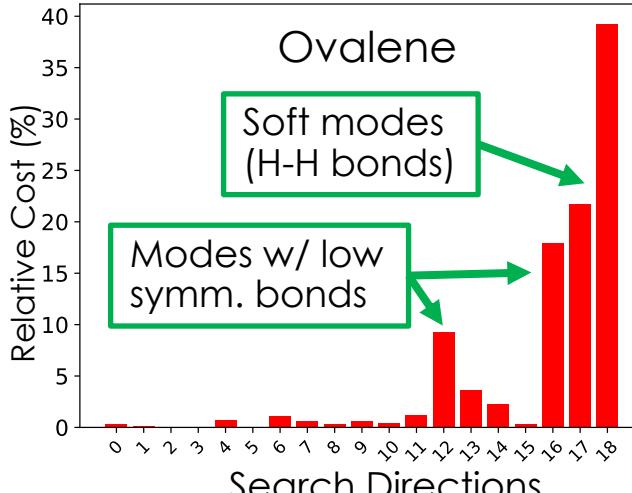
Ovalene Parameters



PES on Search Directions



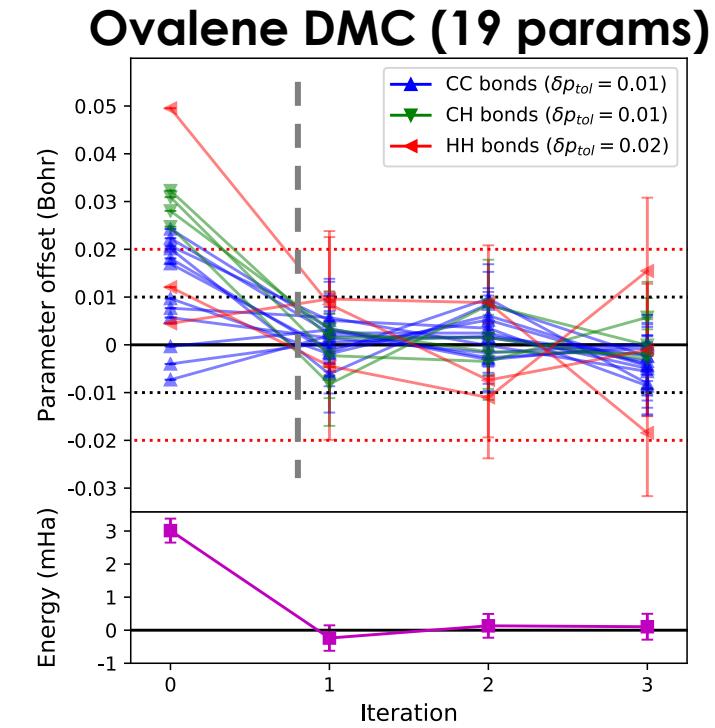
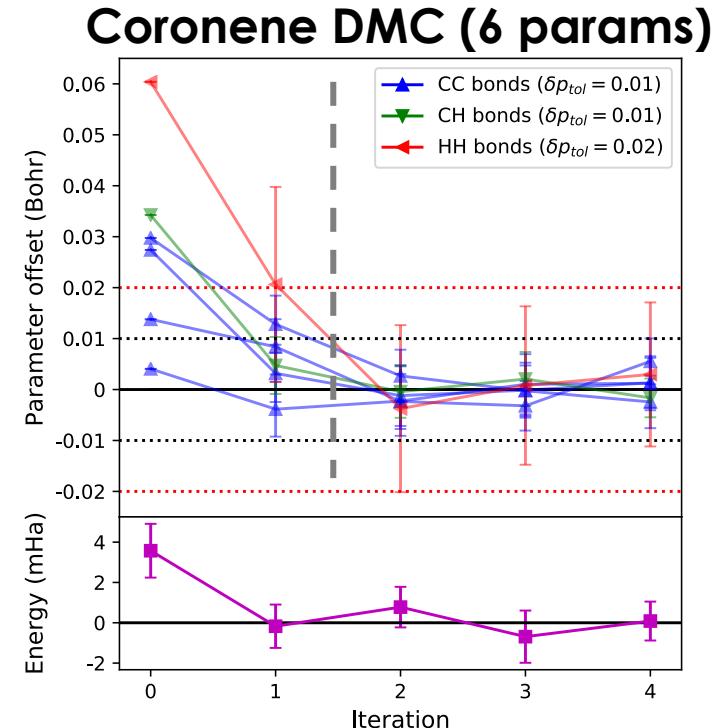
Statistical Cost Per Direction



- Tailored statistics, controlled for bias, leads to low costs for many directions
- Remaining costs dominated by modes w/ low stiffness or low symmetry component bonds

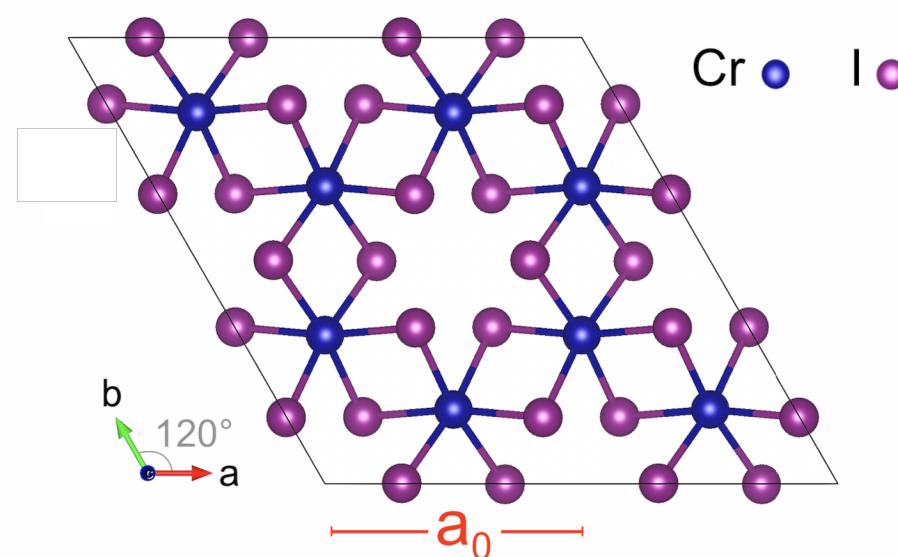
Convergence of Surrogate Hessian Line Search

- Both coronene and ovalene relaxations converge in 1-2 iterations for DMC (independent of parameter count)
- Behavior is very close to the ideal single iteration convergence for pure harmonic PES and perfect search directions
- Near optimal energy-based relaxation algorithm in terms of cost

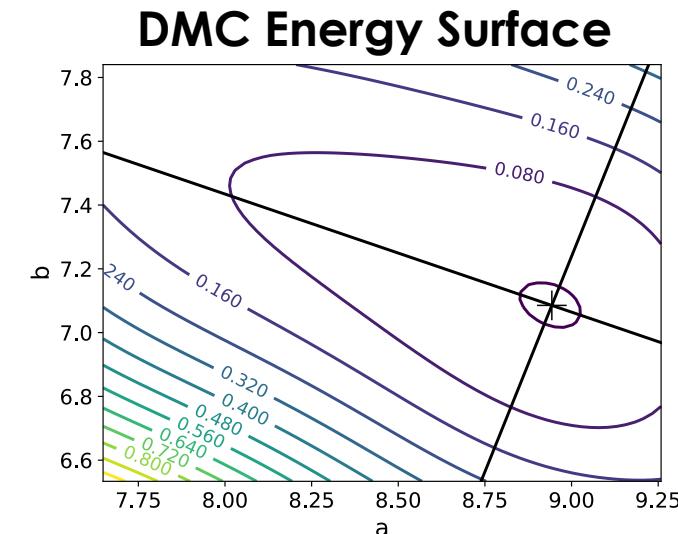
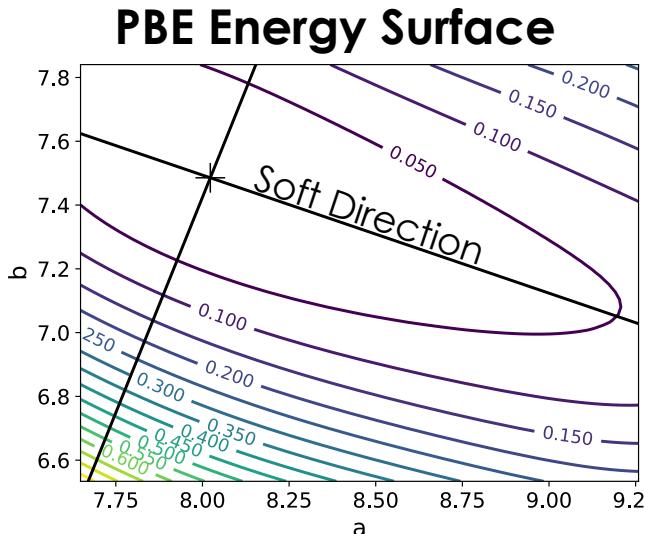
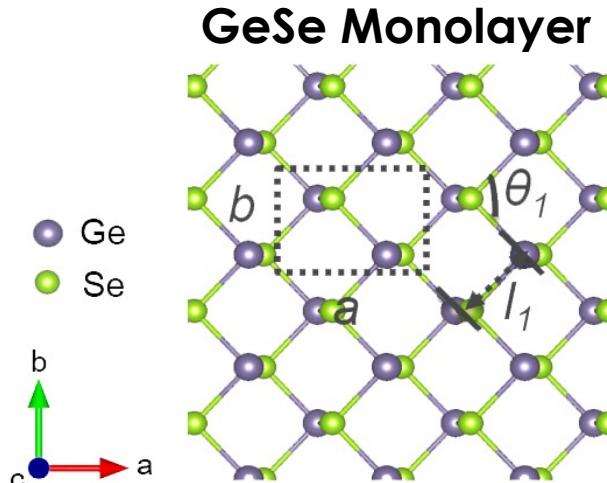


J. Tiihonen, P. R. C. Kent, J. T. Krogel J. Chem. Phys. 156, 054104 (2022)

Application to Quasi-2D Materials

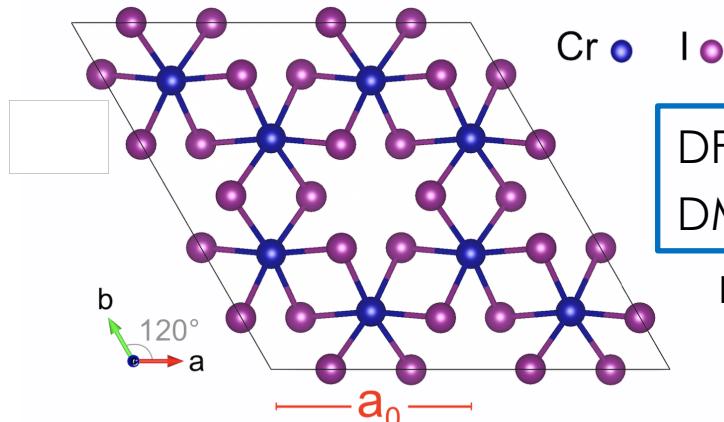


Applications of DMC Relaxation to 2D Materials



H. Shin, J. T. Krogel, K. Gasperich, P. R. C. Kent, A. Benali,
O. Heinonen Phys. Rev. Materials 5, 024002 (2021)

Crl₃ Monolayer



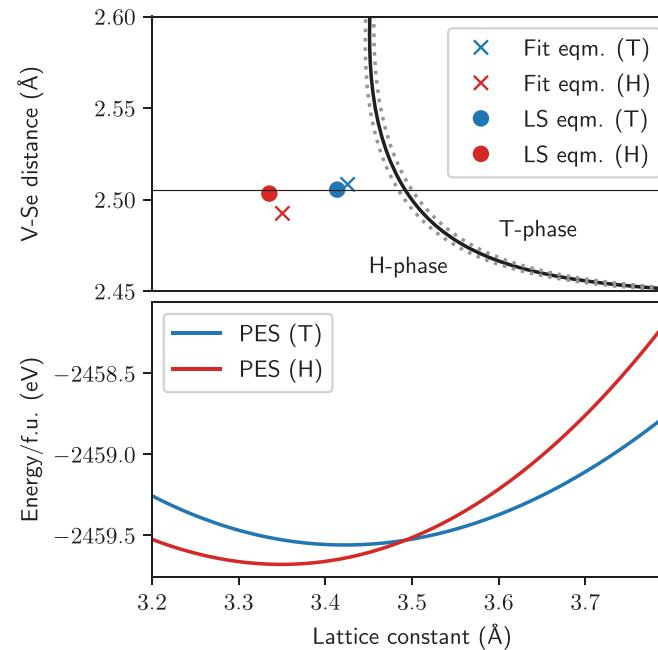
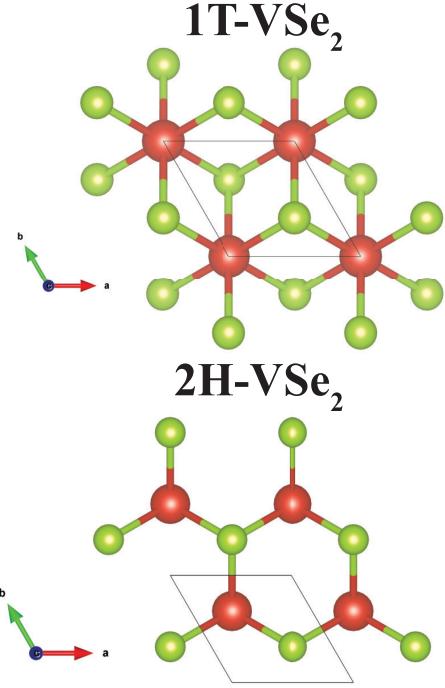
DFT vs. STM: +/- 2.4 % error
DMC vs. STM: 0.4(6) % error

Li Sci. Bulletin 65 1064 (2020)

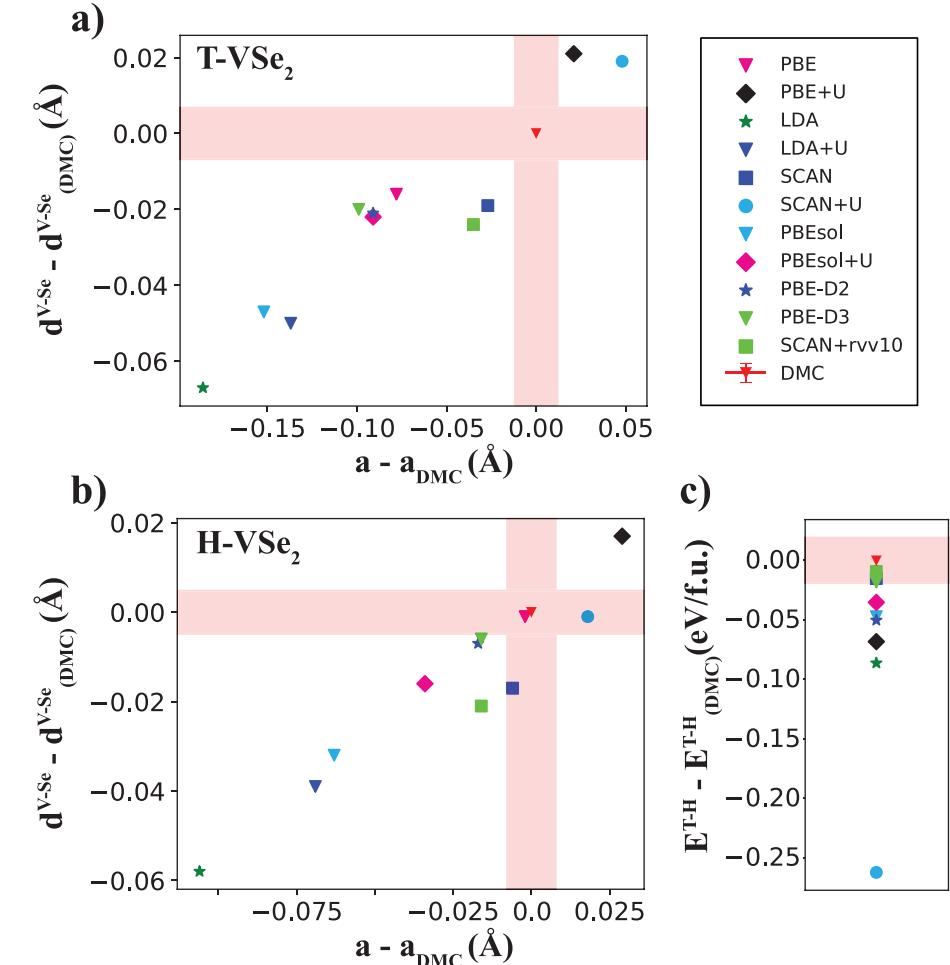
D. Staros, G. Hu, J. Tiihonen, R. Nanguneri, J. T. Krogel, M. C. Bennett,
O. H. Heinonen, P. Ganesh, B. Rubenstein J. Chem. Phys. 156, 014707 (2022)

- GeSe band structure shows great sensitivity to structural parameters
- Though DFT generally insufficiently accurate, PES conjugate directions reasonably represented
- DMC structural optimization of ML Crl₃ shows 5x reduction of errors vs DFT methods

Applications of DMC Relaxation to 2D Materials



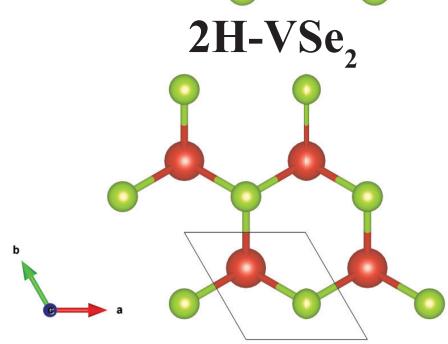
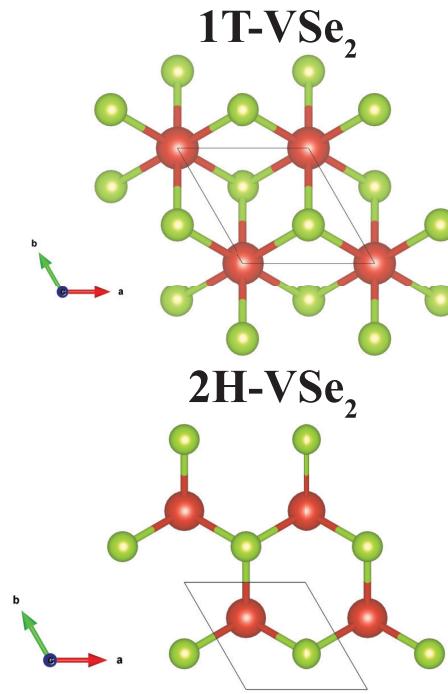
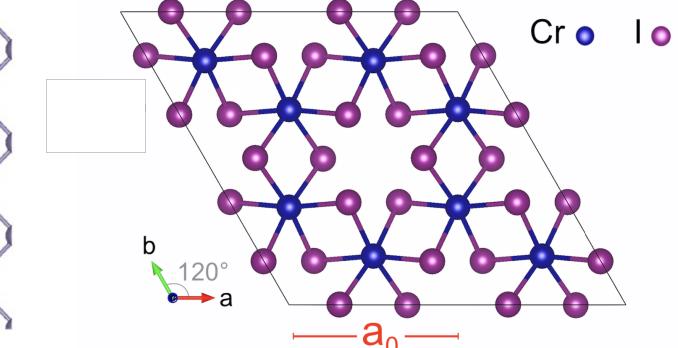
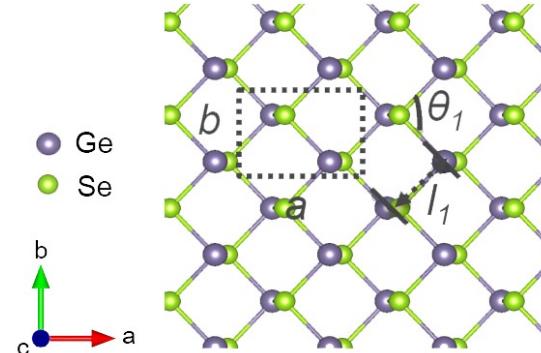
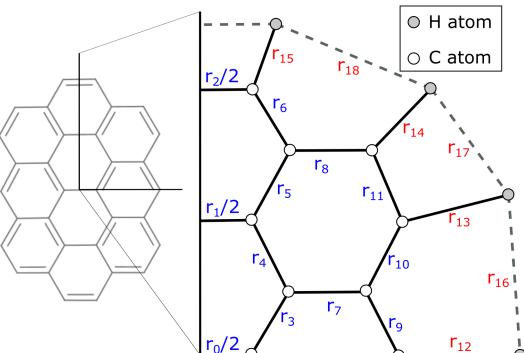
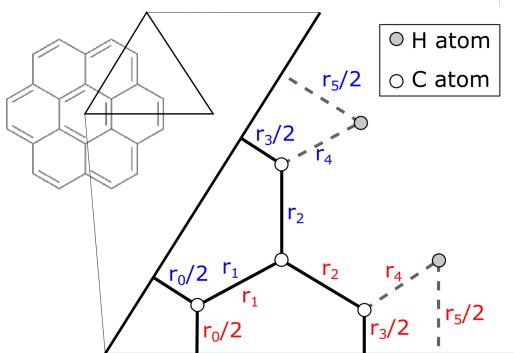
- VSe₂ FM quasi-2D material w/ high Curie Temp. (300-470K)
- Experimental controversy over VSe₂ ground state: 1T (metal) or 2H (semiconductor)
- Large variation in geometry and energy ordering in DFT
- Relaxed DMC geometries establish 2H as ground state, but 1T may be stabilized with strain, depending on the substrate



D. Wines, J. Tiihonen, K. Saritas, J. T. Krogel, C. Ataca J. Phys. Chem. Lett. 14, 3553 (2023)

Summary and Outlook

- Developed energy based structural optimization method for stochastic electronic structure theories
- Method exploits approximate, but accurate, Hessian information from DFT as a surrogate theory
- Method explicitly maximizes statistical efficiency while retaining controllable accuracy
- In practice, convergence achieved in 1-2 iterations for 2D systems: benzene, coronene, ovalene, GeSe, CrI₃, VSe₂
- Useful as a simple but efficient approach, e.g. cell degrees of freedom handled as easily as others



Open slide master to edit

GitHub Repository & Example



Surrogate Hessian Relax GitHub Repository

https://github.com/QMCPACK/surrogate_hessian_relax

The screenshot shows the GitHub repository page for 'surrogate_hessian_relax'. The repository is owned by QMCPACK. The main navigation bar includes links for Code, Issues, Pull requests, Actions, Projects, Wiki, Security, Insights, and Settings. The 'Code' tab is selected. On the left, the file tree shows the directory structure: master (docs, examples, legacy, lib, sphinx, tests, .gitignore, LICENSE). The 'examples' folder contains files like benzene.py, coronene.py, download_pseudos.sh, morse_3p.py, nxs.py, README.md, and overview.png. The right side displays the README.md file, which is titled 'Surrogate Hessian Relax'. It describes the method as a Python implementation of the Surrogate Hessian Accelerated Parallel Line-search for atomic structures. A note states that the implementation is in an early stage of development. Below this, a section titled 'ORIGINAL WORK' cites a publication in The Journal of Chemical Physics: Juha Tiihonen, Paul R. C. Kent, and Jaron T. Krogel, 156, 054104 (2022).

QMCPACK / surrogate_hessian_relax

Type to search

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Files

master

Go to file

docs

examples

- benzene.py
- coronene.py
- download_pseudos.sh
- morse_3p.py
- nxs.py
- README.md
- overview.png

legacy

lib

sphinx

tests

.gitignore

LICENSE

surrogate_hessian_relax / README.md

jtkrogel Update README.md 90567e0 · 2 years ago History

Preview Code Blame 113 lines (76 loc) · 4.42 KB

Raw

Surrogate Hessian Relax

Surrogate Hessian Relax is a Python implementation of The Surrogate Hessian Accelerated Parallel Line-search. The method is intended for optimizing and performing energy minimization of atomic structures in the presence of statistical noise.

NOTE: the implementation is currently in an early stage of development.

ORIGINAL WORK

The method has been published in The Journal of Chemical Physics as [Surrogate Hessian Accelerated Structural Optimization for Stochastic Electronic Structure Theories](#)

Upon publishing results based on the method, we kindly ask you to cite

Juha Tiihonen, Paul R. C. Kent, and Jaron T. Krogel
The Journal of Chemical Physics
156, 054104 (2022)

Running Surrogate Hessian Relaxation on a Model System

https://github.com/QMCPACK/qmcpack_workshop_2023/tree/main/day2_surr_hess_relax

qmcpack_workshop_2023 / day2_surr_hess_relax / ↑ Top

README.md Edit

Surrogate Hessian Structure Optimization on an Artificial PES

Example description

Artificial model involving three coupled Morse oscillators.

Surrogate and actual PES's represented by different (but related) coupled Morse oscillator systems.

Deterministic structural relaxation along the surrogate PES performed with numerical methods in scipy rather than DFT.

The full surrogate hessian parallel line search algorithm is performed on the actual PES (different from the surrogate) with added statistical noise to represent DMC.

Installation requirements

- Standard Python libraries needed: numpy, dill, scipy, matplotlib
 - pip3 install numpy
 - pip3 install dill
 - pip3 install scipy
 - pip3 install matplotlib
- Nexus
 - git clone <https://github.com/QMCPACK/qmcpack.git>
 - export PYTHONPATH=/your/path/to/qmcpack/nexus/lib:\$PYTHONPATH
- Surrogate Hessian Relax
 - git clone https://github.com/QMCPACK/surrogate_hessian_relax.git
 - export PYTHONPATH=/your/path/to/surrogate_hessian_relax:\$PYTHONPATH

Surrogate Hessian Relax GitHub Repository

https://github.com/QMCPACK/qmcpack_workshop_2023/tree/main/day2_surr_hess_relax

Running the example

./morse_3p.py

What to look for

- Minimum energy parameters of the surrogate PES ("DFT" structure)
- Details of the surrogate hessian (note degree of coupling)
- User defined parameter tolerances (requested parameter accuracy)
- Convergence of parameters with parallel iteration count (also note error bars on/statistical uncertainty of the parameters)
- (analytic/reference) minimum energy parameters of the actual PES ("DMC" structure), and how they compare with the parameters found via line search (including statistical uncertainty)

```
=====
Surrogate PES: obtain relaxed geometry and surrogate Hessian ("DFT")
=====

Minimum-energy parameters (surrogate):
[1.38044924 2.29368731 3.08427957]

Surrogate Hessian:
ParameterHessian
hessian:
 0.161745 0.032602 0.054581
 0.032602 0.287088 0.097587
 0.054581 0.097587 0.922804
Conjugate directions:
  Lambda      Direction
 0.941886   +0.075260 +0.150652 +0.985718
 0.152480   +0.977712 -0.205448 -0.043249
 0.277271   -0.195998 -0.967003 +0.162757

=====
Tune/design parallel line search process (minimize cost)
=====

=====
Perform parallel line search ("DMC")
=====

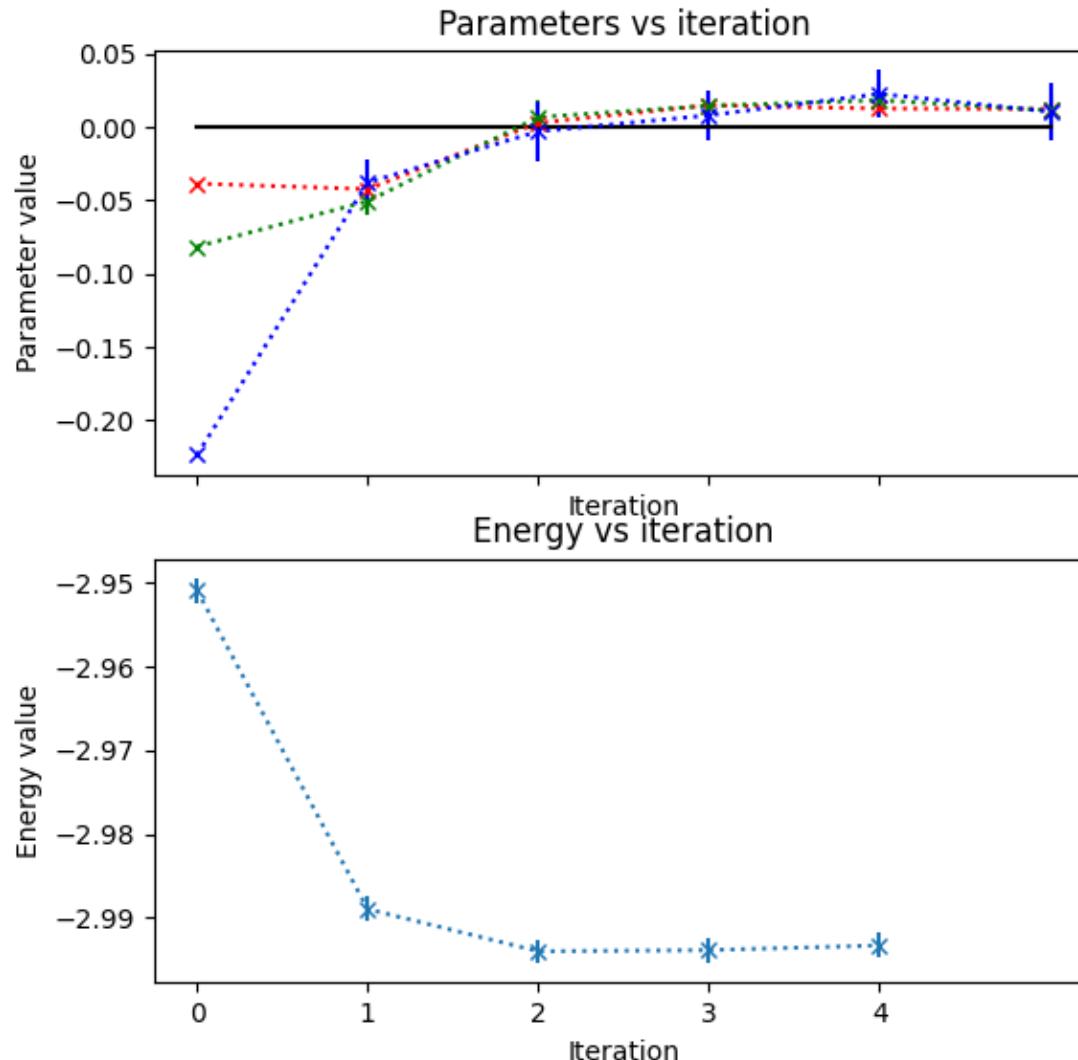
Linesearch diagnostics:

Parameter convergence:
pls0  1.380449 +/- 0.000000 2.293687 +/- 0.000000 3.084280 +/- 0.000000
pls1  1.376650 +/- 0.005189 2.324599 +/- 0.009620 3.269886 +/- 0.015181
pls2  1.421858 +/- 0.004928 2.381868 +/- 0.011273 3.304762 +/- 0.020253
pls3  1.433806 +/- 0.005115 2.389600 +/- 0.008499 3.315701 +/- 0.016754
pls4  1.431555 +/- 0.005185 2.393369 +/- 0.011233 3.330304 +/- 0.016548
pls5  1.441963 +/- 0.005374 2.384939 +/- 0.009615 3.328533 +/- 0.019227

=====
Minimum-energy parameters (actual/reference):
=====
[1.43985799 2.40038018 3.32983772]
param tolerances: [0.01, 0.02, 0.03]
```

Surrogate Hessian Relax GitHub Repository

https://github.com/QMCPACK/qmcpack_workshop_2023/tree/main/day2_surr_hess_relax



```
=====
Surrogate PES: obtain relaxed geometry and surrogate Hessian ("DFT")
=====
Minimum-energy parameters (surrogate):
[1.38044924 2.29368731 3.08427957]

Surrogate Hessian:
ParameterHessian
hessian:
 0.161745 0.032602 0.054581
 0.032602 0.287088 0.097587
 0.054581 0.097587 0.922804
Conjugate directions:
  Lambda   Direction
 0.941886  +0.075260 +0.150652 +0.985718
 0.152480  +0.977712 -0.205448 -0.043249
 0.277271  -0.195998 -0.967003 +0.162757
=====

Tune/design parallel line search process (minimize cost)
=====

Perform parallel line search ("DMC")
=====

Linesearch diagnostics:

Parameter convergence:
pls0  1.380449 +/- 0.000000 2.293687 +/- 0.000000 3.084280 +/- 0.000000
pls1  1.376650 +/- 0.005189 2.324599 +/- 0.009620 3.269886 +/- 0.015181
pls2  1.421858 +/- 0.004928 2.381868 +/- 0.011273 3.304762 +/- 0.020253
pls3  1.433806 +/- 0.005115 2.389600 +/- 0.008499 3.315701 +/- 0.016754
pls4  1.431555 +/- 0.005185 2.393369 +/- 0.011233 3.330304 +/- 0.016548
pls5  1.441963 +/- 0.005374 2.384939 +/- 0.009615 3.328533 +/- 0.019227
=====

Minimum-energy parameters (actual/reference):
=====
[1.43985799 2.40038018 3.32983772]
param tolerances: [0.01, 0.02, 0.03]
```

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Electronic Structure Packages

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