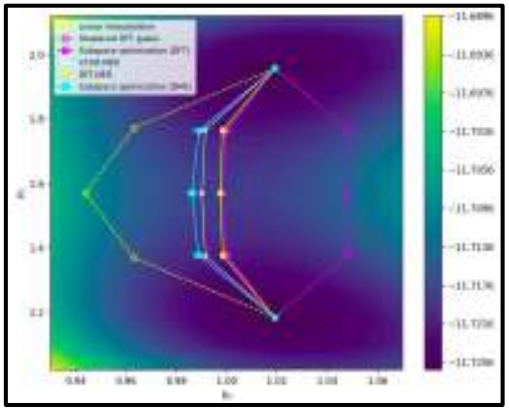
# EXTENDING THE REACH OF QMC VIA SURROGATE METHODS

'QMC Forces'

Minimum Energy Pathways



D. Staros *et al.*, JCP (2022); G. Iyer *et al.*, JPCA (2022); G. Iyer *et al.*, JCTC (2024); C. Huang *et al.*, JPCA (2023).


**PROF. BRENDA RUBENSTEIN**

**Associate Professor of Chemistry and Physics**

*TREX, Spring 2024*

BROWN

*brenda_rubenstein@brown.edu*

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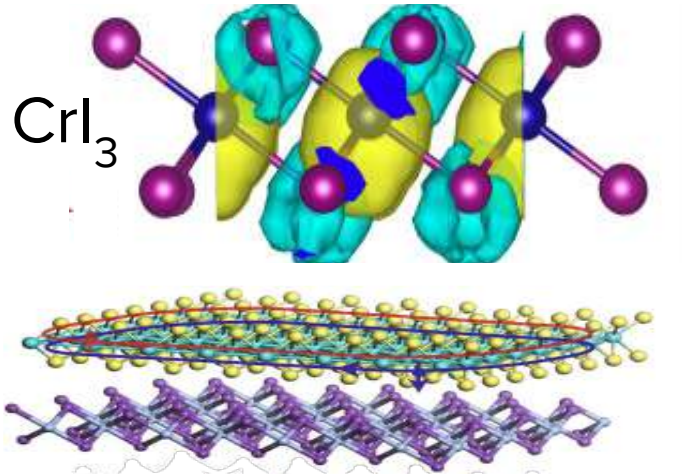
# THE RUBENSTEIN GROUP @ BROWN

## Theoretical/Computational Chemistry and Physics

### DMC of Quantum Materials (w/ CPSFM)




*Ab Initio Description of Magnetism and Topology in Quantum Materials*

*D. Staros, npj Spintronics (2024).*

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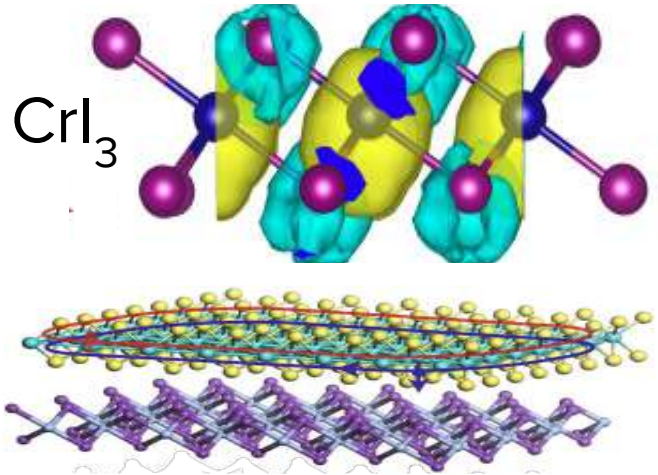


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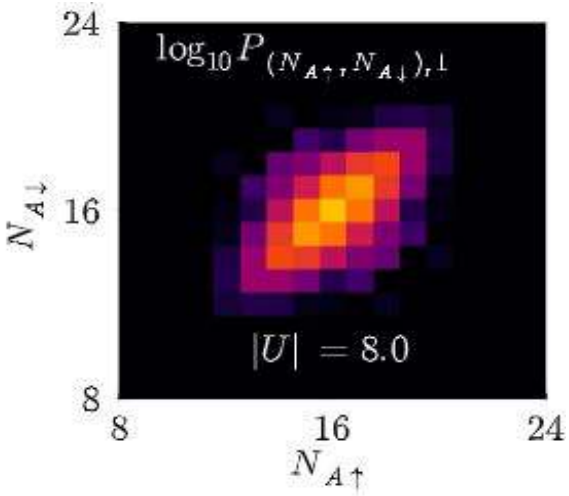


*Predicting Symmetry-Resolved Entanglement Efficiently*

*T. Shen et al., arXiv:2312.11746 (2023).*

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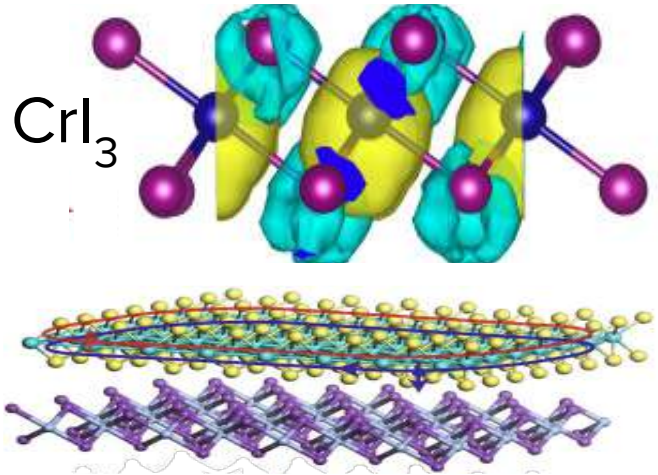


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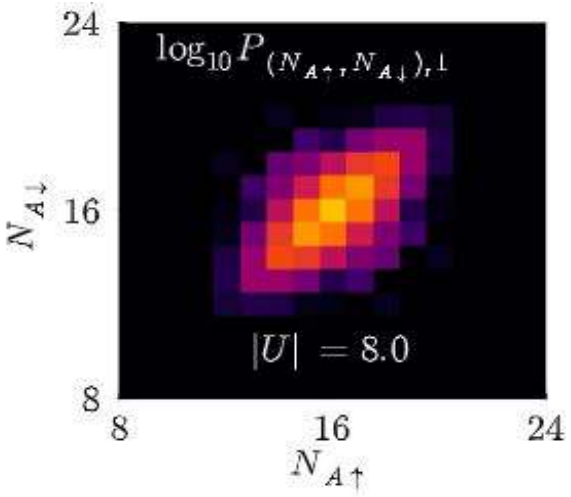


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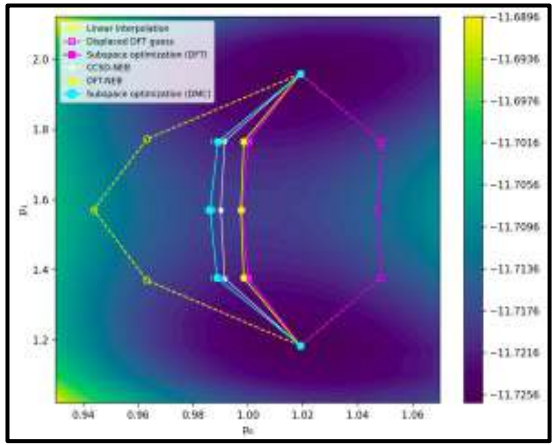

*Enabling DMC-Based Chemical Reaction Dynamics*

*G. Iyer, To appear (2024).*

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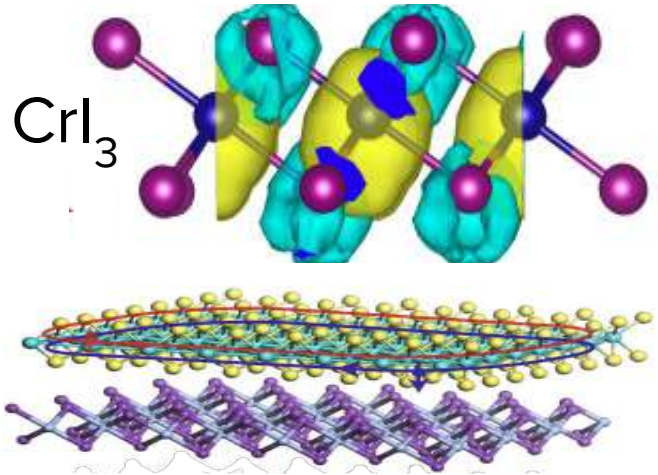


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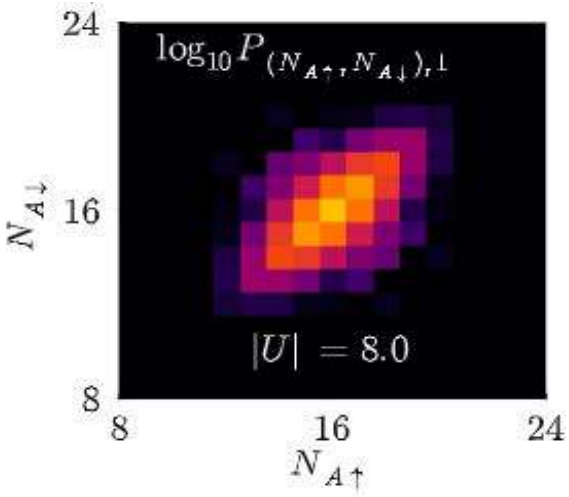


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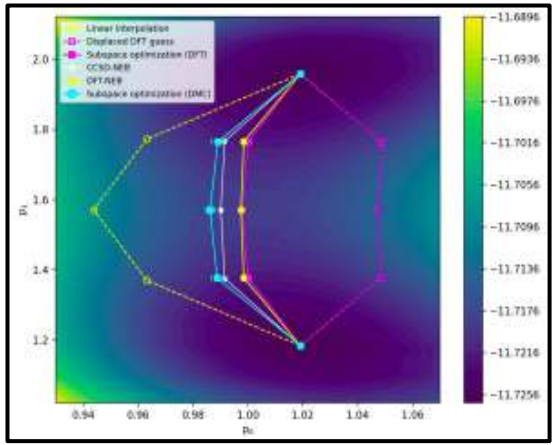

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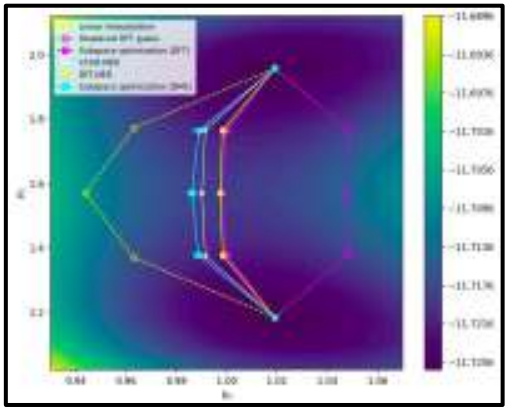

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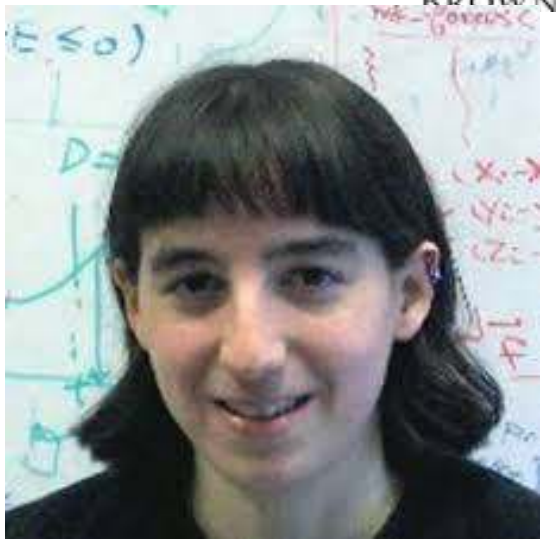
# AN INSPIRATIONAL FORCE ~2006

Me: I'm thinking about working on quantum Monte Carlo methods.

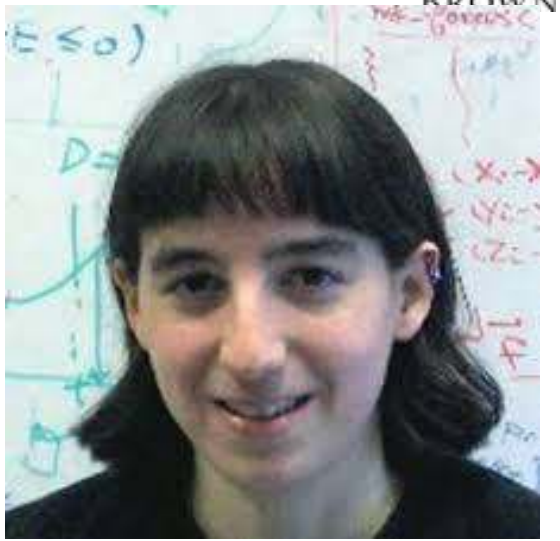


Bruce Berne
(Columbia)

Bruce: That's nice, but you'll never be able to do any chemistry. Just H and He, which *isn't* chemistry. And QMC has no forces, so good luck with reactions.

# AN INSPIRATIONAL FORCE ~2006

Me: => I guess I'll do QMC then.



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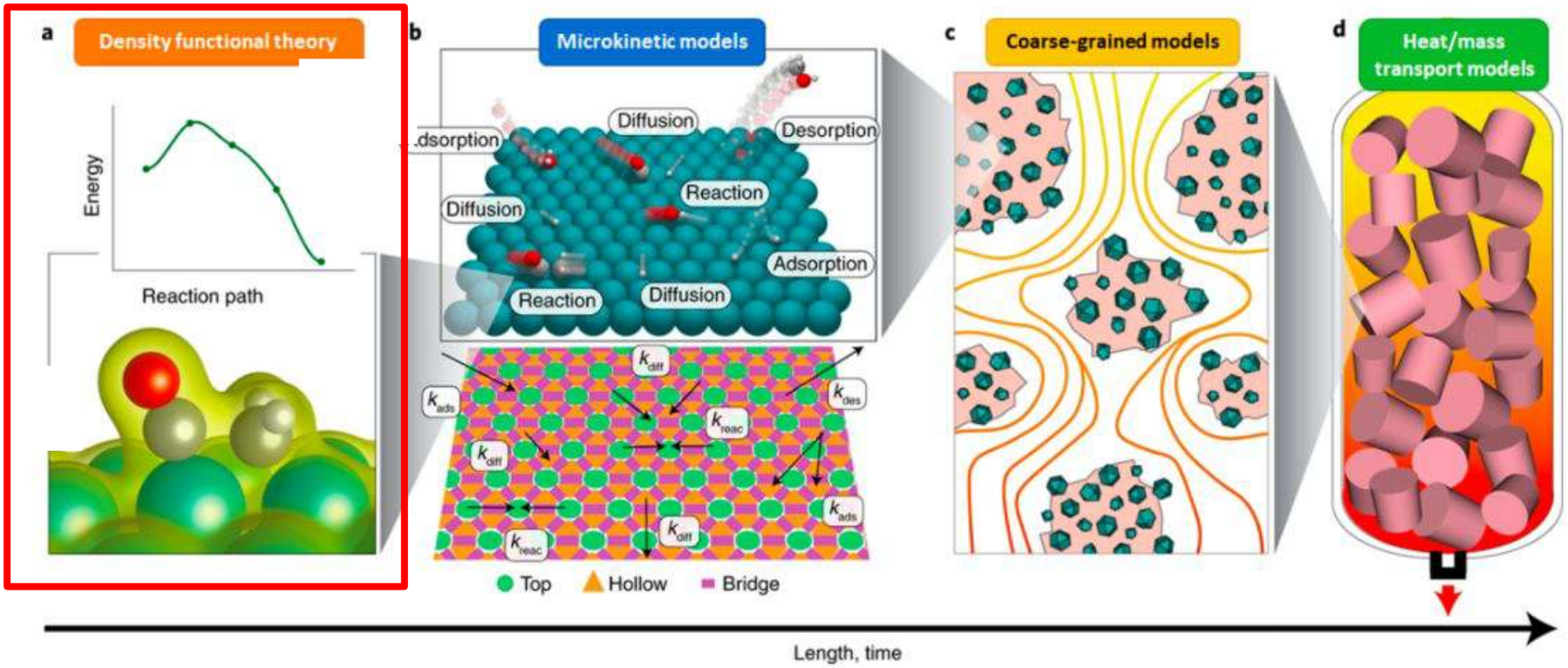
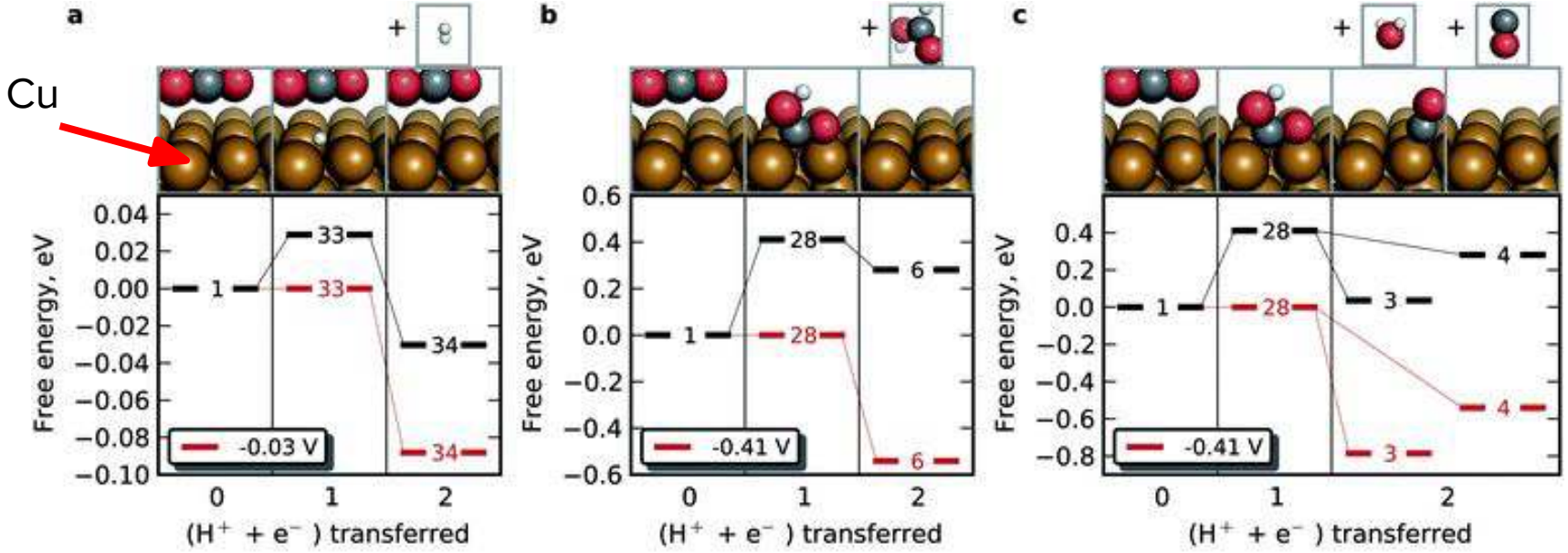
# MOST OF MODERN-DAY ~~CATALYSIS~~CHEM




Density functional theory has become the computational workhorse for catalysis, informing mechanisms and microkinetic models, *BUT...*

*B. Chen and M. Mavrikakis, Chem. Reviews* (2021).

# MOST OF MODERN-DAY CATALYSIS




$CO_2 \rightarrow H_2$ $CO_2 \rightarrow HCOOH$ $CO_2 \rightarrow H_2O + CO$ Evolution

Density functional theory has become the computational workhorse for catalysis, informing mechanisms and microkinetic models, *BUT...*

*A. Peterson and J. Norskov, Energy Environ. Sci.* (2010).

# CORRELATION IN CATALYSIS

## But Correlation Is Widely Prevalent…and Important

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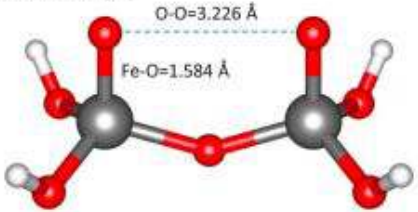
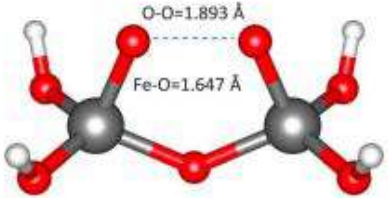
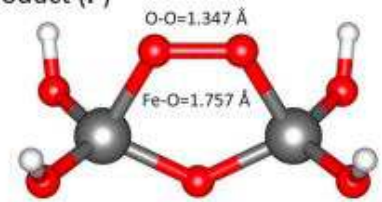
a) Reactant (**R**)



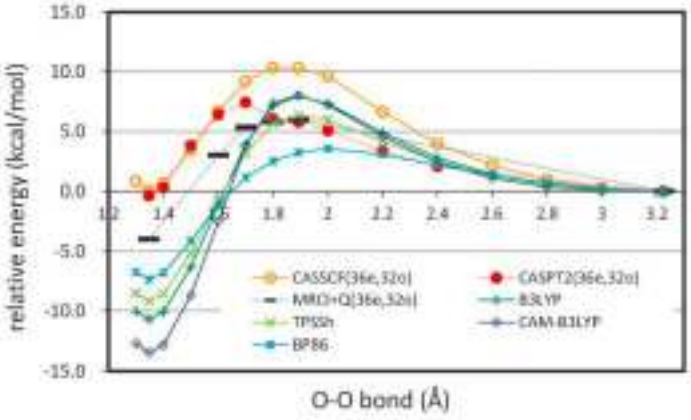

b) Transition state (**TS**)



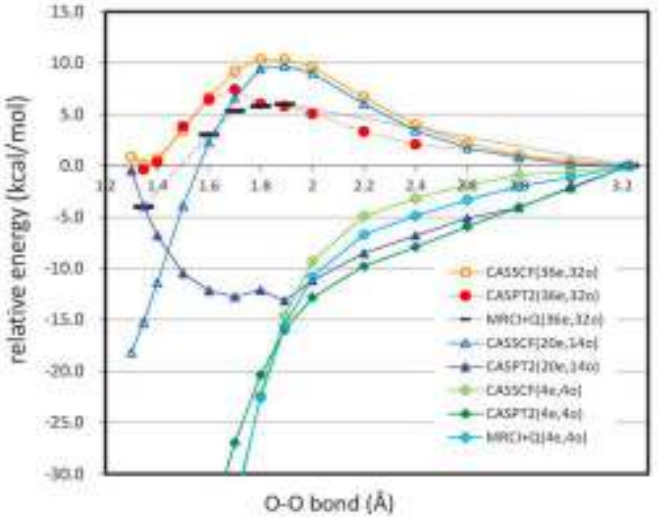

c) Product (**P**)




Diferrate, $[H_4Fe_2O_7]^{2+}$




Variance Among DFT Functionals




Variance Among Multireference Theories

*Y. Kurashige et al., PCCP* (2014).

# MOST OF MODERN-DAY CATALYSIS

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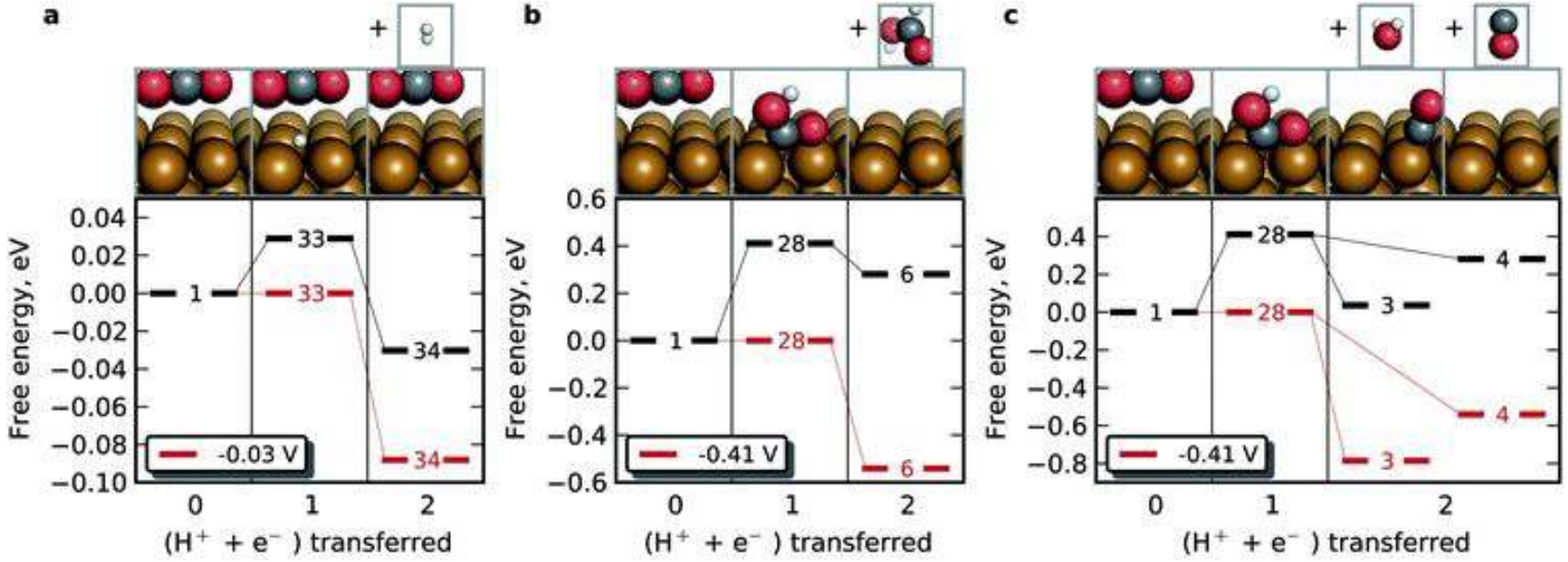
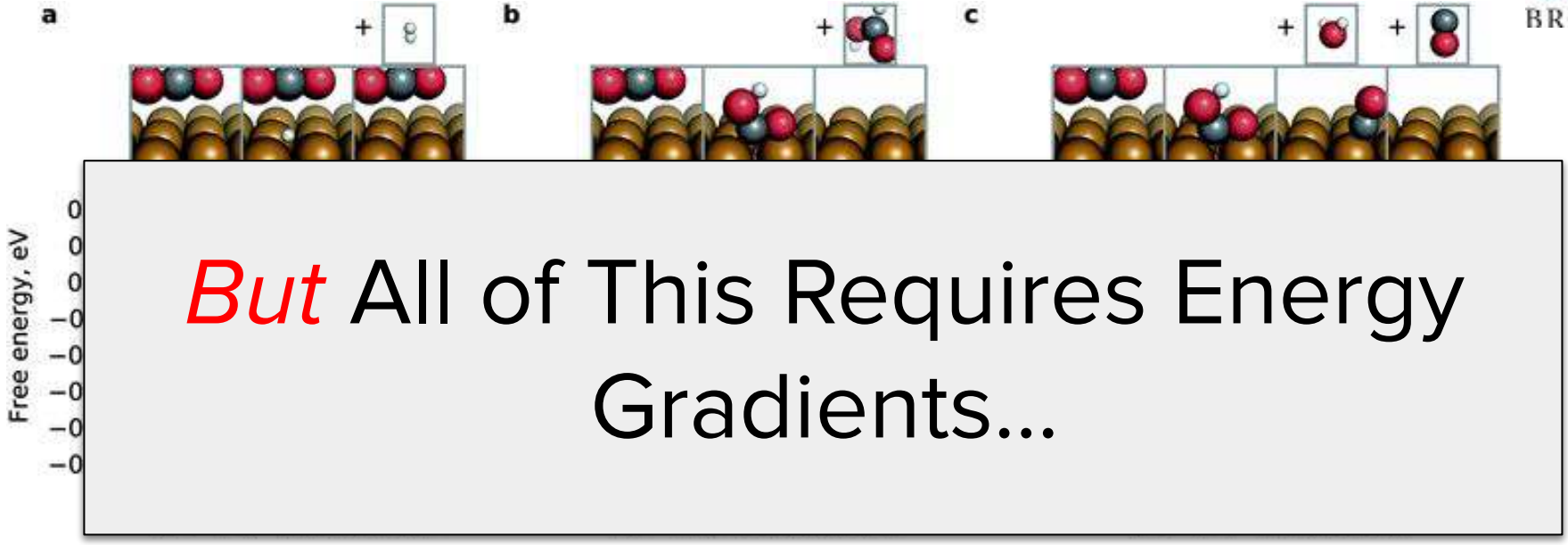



A WISH LIST *to even begin* down the road toward catalysis:

| Equilibrium Geometries | Transition States | Reaction Pathways | Chemical Dynamics |
|---|---|---|---|

# MOST OF MODERN-DAY CATALYSIS




*But* All of This Requires Energy Gradients…

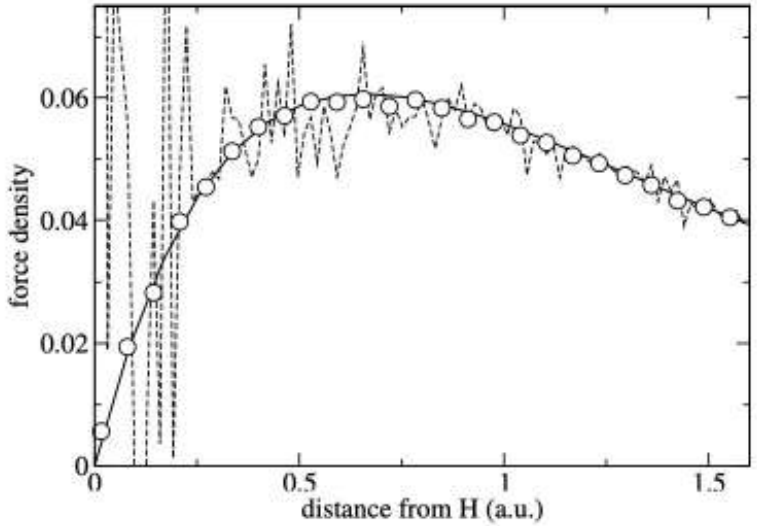
A WISH LIST *to even begin* down the road toward catalysis:

| Equilibrium Geometries | Transition States | Minimum Energy Pathways | Thermodynamic Corrections |
|---|---|---|---|

# ENERGY GRADIENTS REMAIN A CHALLENGE

## But Are Essential if QMC Is To Shed Light on 'Real' Chemistry

- DMC forces have long been challenging
  - Infinite Variance Problems
- But, much progress has been made on Zero-Variance, Zero-Bias Estimators
  - Assaraf, Caffarel, Filippi, Moroni, Krogel, Nakano, Casula, others…
- Nonetheless, they often remain very expensive and lack easy access to DMC Hessians (exc. Filippi, Moroni, *et al.*)

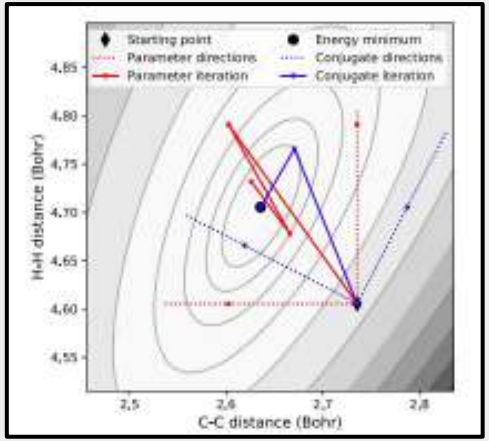



*S. Chiesa et al., PRL* (2005).

# TODAY'S OUTLINE

## SURROGATE METHODS

Surrogate
Hessian
Line
Search



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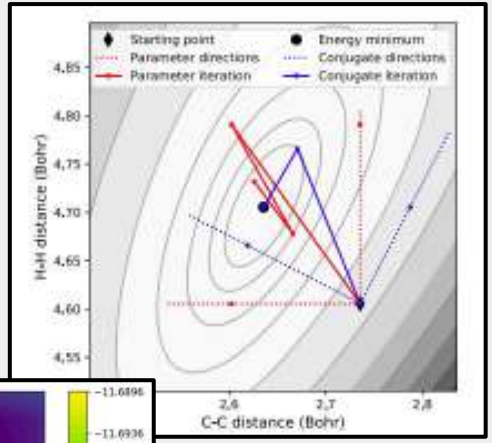
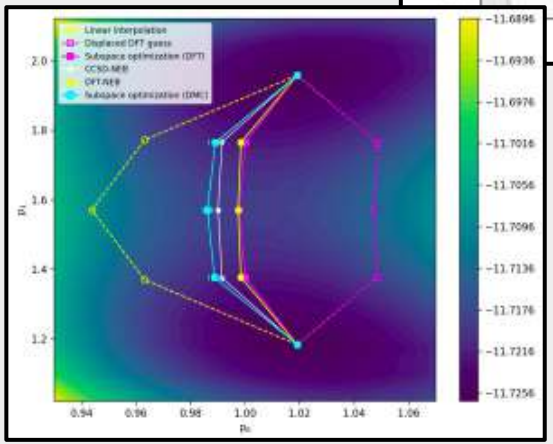


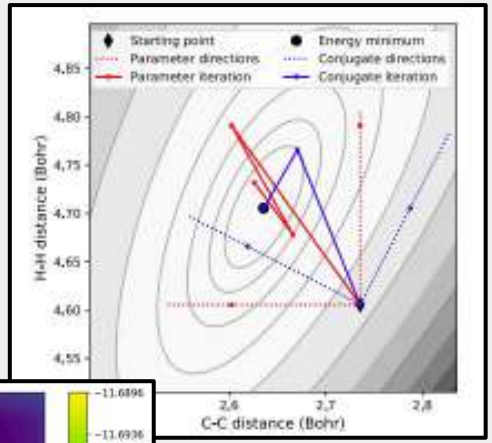



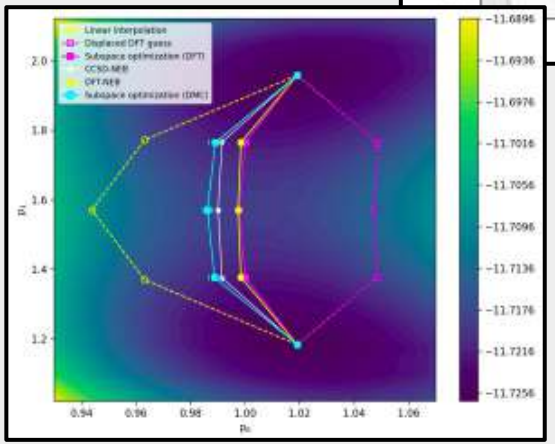
Minimum
Energy
Pathways

# TODAY'S OUTLINE

## SURROGATE METHODS

Surrogate Hessian Line Search



Minimum Energy Pathways

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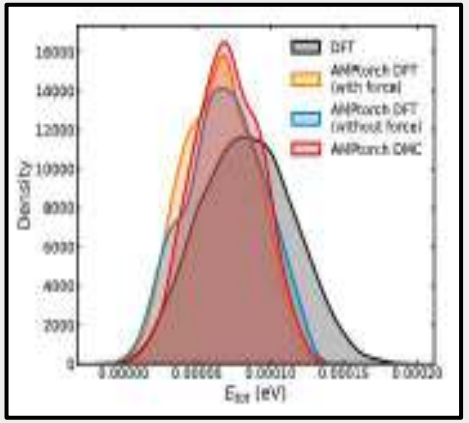
QMC Dynamics with BPNNS



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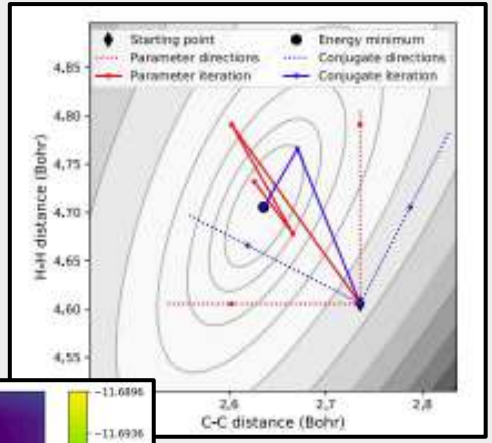


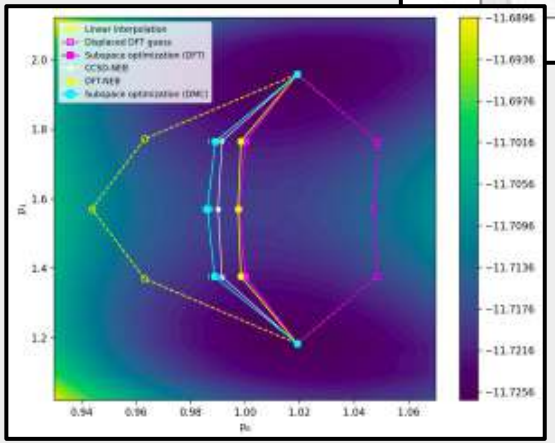

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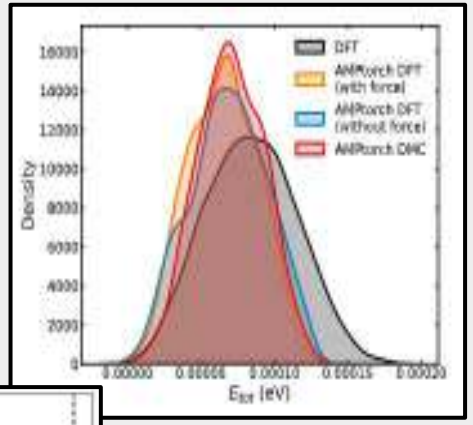
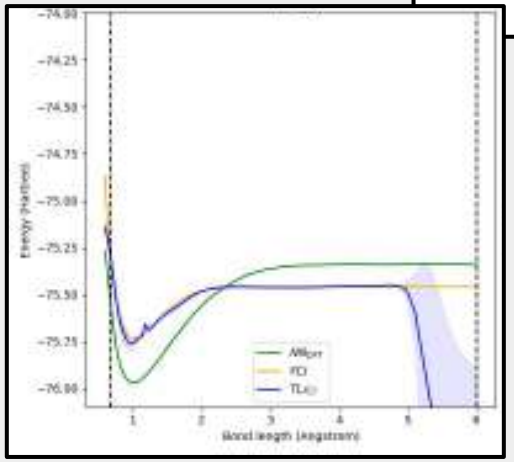
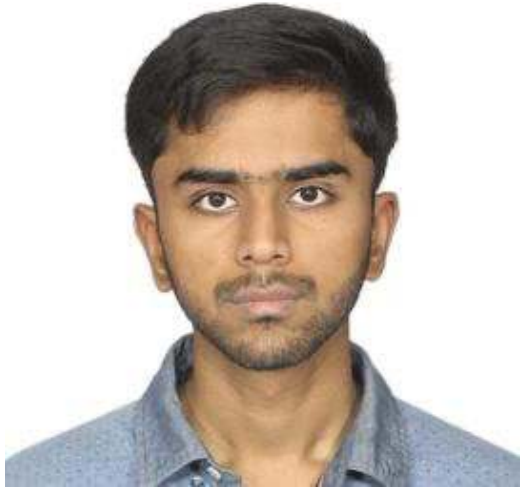



Transfer Learning

# ACKNOWLEDGEMENTS



Gopal Iyer
(Brown)
5th-YearChemistry PhD Student
(Soon to be NREL)

Jaron Krogel
(Oak Ridge)

+

CPSFM

# SURROGATE METHODS FOR FORCES

# SURROGATE HESSIAN LINE SEARCH

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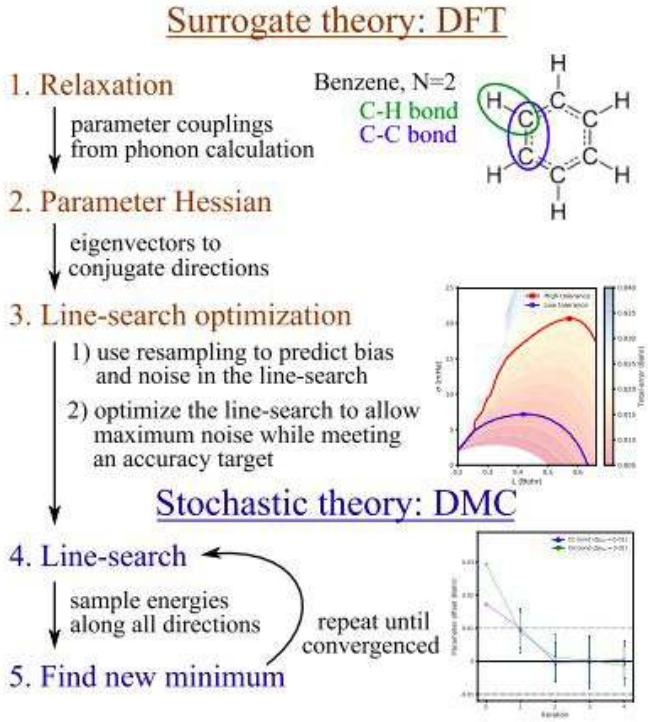
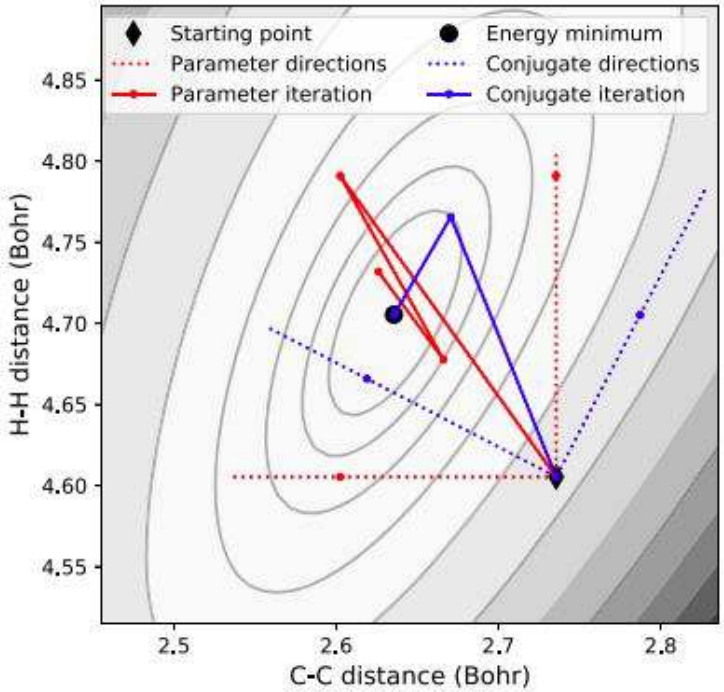
## Surrogate Hessian Structure Optimization




- Uses DFT to Accelerate DMC-Level Geometry Optimization

*D. Staros, B. Rubenstein, et al., JCP (2022); J. Tiihonen et al., JCP (2021).*

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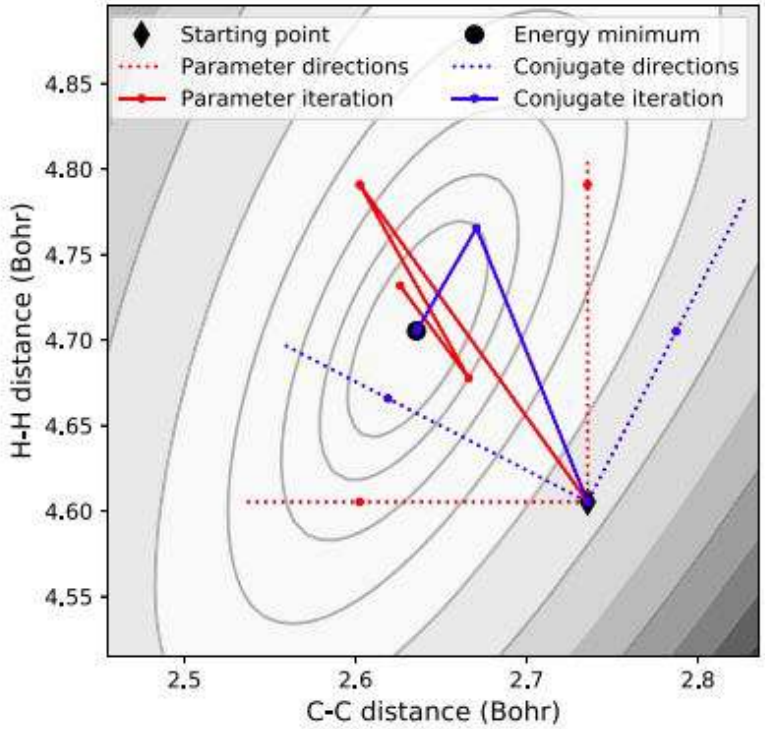


### The Hessian and Conjugate Directions

$$E(p) = E_0 + \frac{1}{2}(p - p_0)^T H_p (p - p_0)$$

*D. Staros, B. Rubenstein, et al., JCP (2022); J. Tiihonen et al., JCP (2021).*

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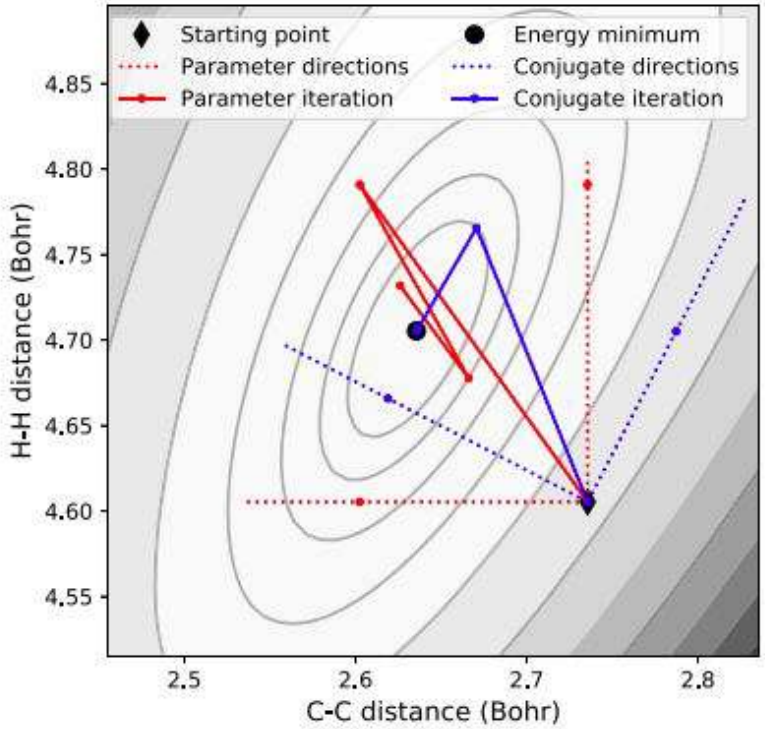


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$$= E_0 + \frac{1}{2} x^T \Lambda x$$

$$= E_0 + \frac{1}{2} \sum_{n=1}^{N} \lambda_n x_n^2.$$

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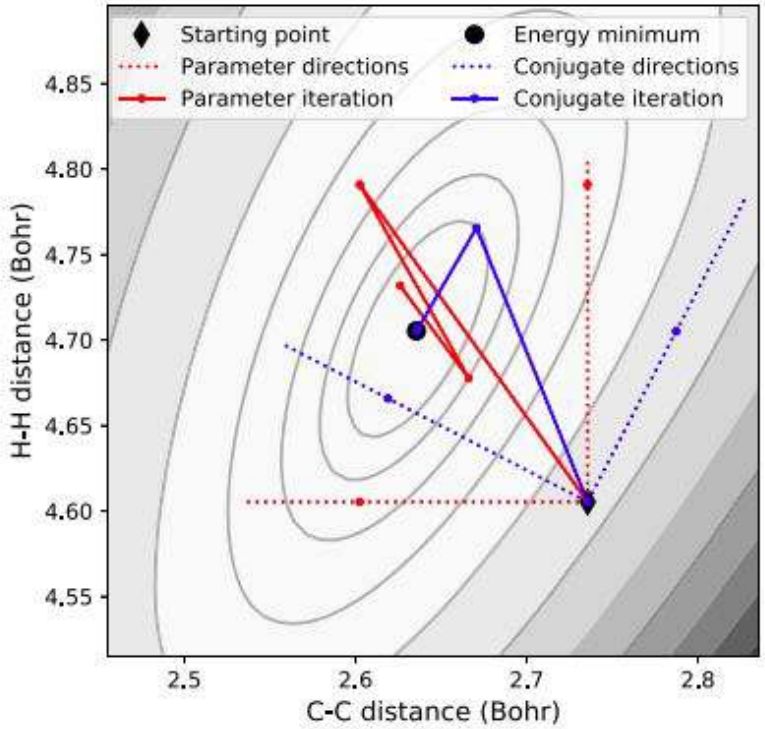


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$$= E_0 + \frac{1}{2} x^T \Lambda x$$

$$= E_0 + \frac{1}{2} \sum_{n=1}^{N} \lambda_n x_n^2.$$

### Parallel Search Along Directions

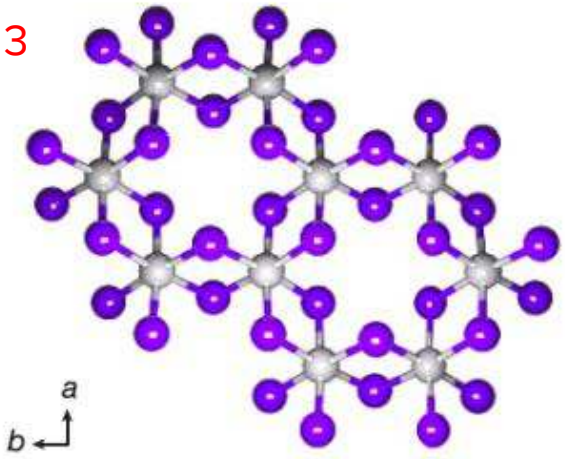
$$p(x_n) = \bar{p}_n + d_n x_n$$

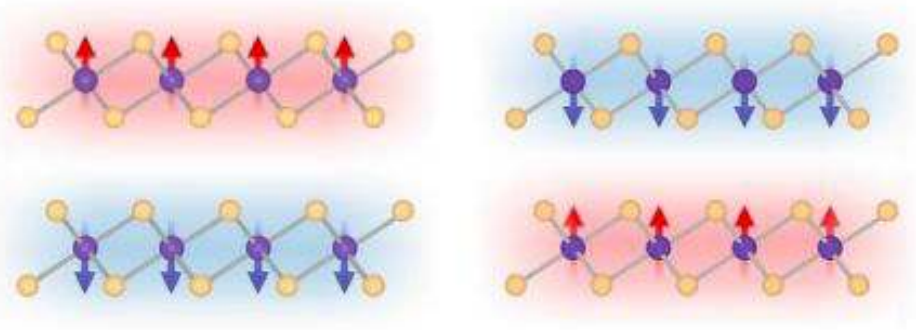
$$x_{0n} = \arg\min_{x_n} E(\bar{p}_n + d_n x_n)$$

*D. Staros, B. Rubenstein, et al., JCP (2022); J. Tiihonen et al., JCP (2021).*

# EXAMPLE: THE ML FERROMAGNET $CrI_3$

$CrI_3$



AFM Order in Bilayers

**$CrI_3$: Member of class of chromium trihalides ($CrX_3$)**

- **First discovered 2D monolayer ferromagnet** - *but becomes an antiferromagnet* when layered
- Bulk semiconductor (Band Gap ~1.2 eV)
- Monoclinic structure >240 K; rhombohedral <240 K

*M. McGuire et al., Chem Mat (2015).*

*B. Huang et al., Nature (2018).*

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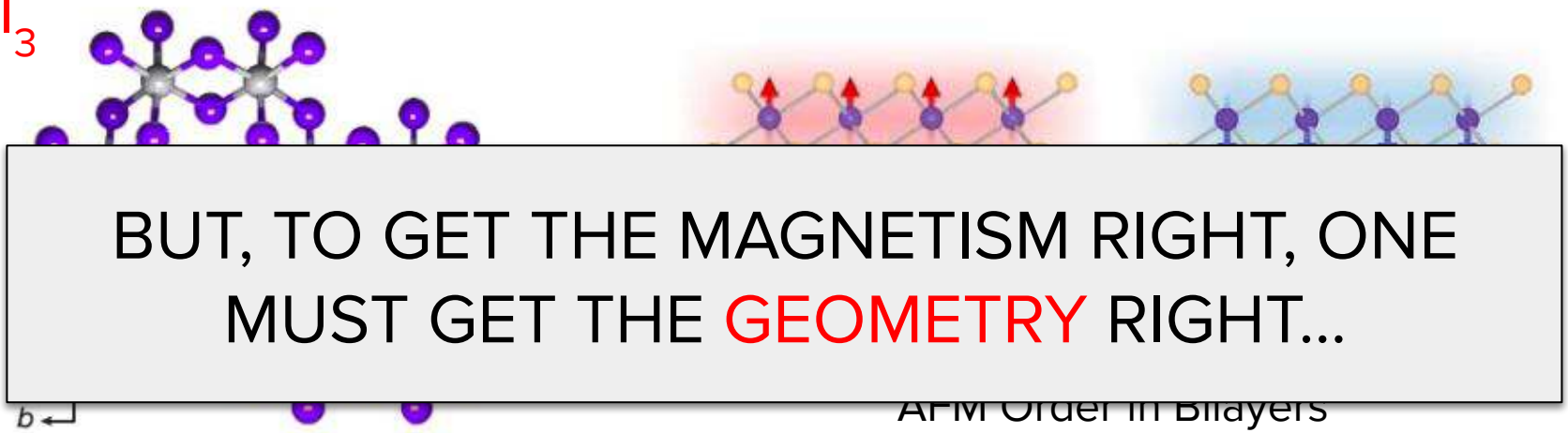
BROWN

$CrI_3$




BUT, TO GET THE MAGNETISM RIGHT, ONE MUST GET THE GEOMETRY RIGHT…

**$CrI_3$: Member of class of chromium trihalides ($CrX_3$)**

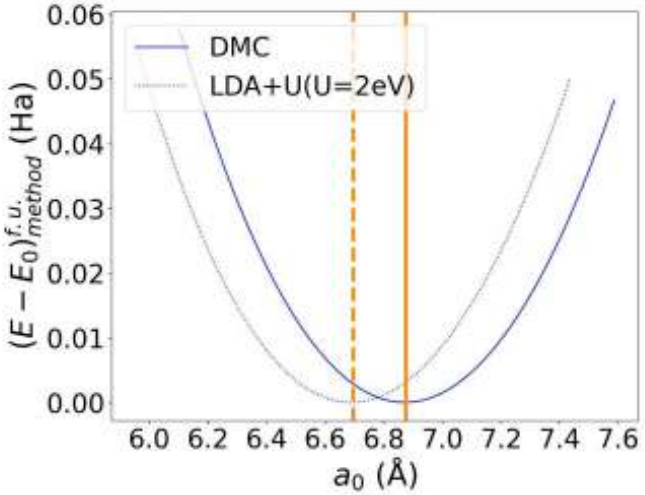
- **First discovered 2D monolayer ferromagnet** - *but becomes an antiferromagnet* when layered
- Bulk semiconductor (Band Gap ~1.2 eV)
- Monoclinic structure >240 K; rhombohedral <240 K

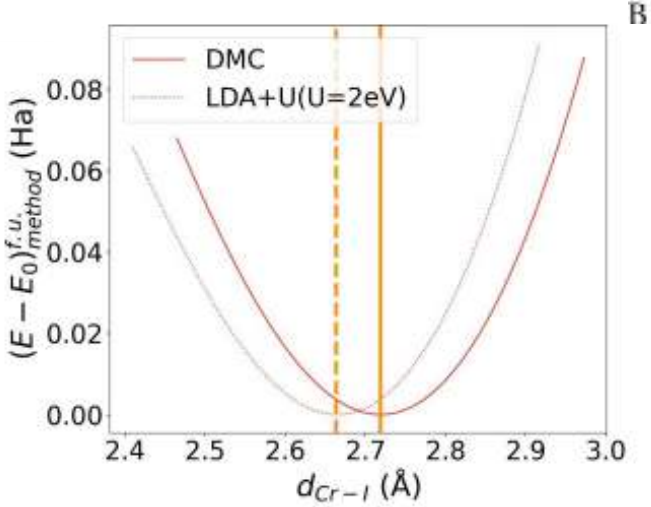
*M. McGuire et al., Chem Mat (2015).*

*B. Huang et al., Nature (2018).*

# MATERIAL GEOMETRY OPTIMIZATION

*Several* Percent Different Lattice Parameters And Bond Lengths



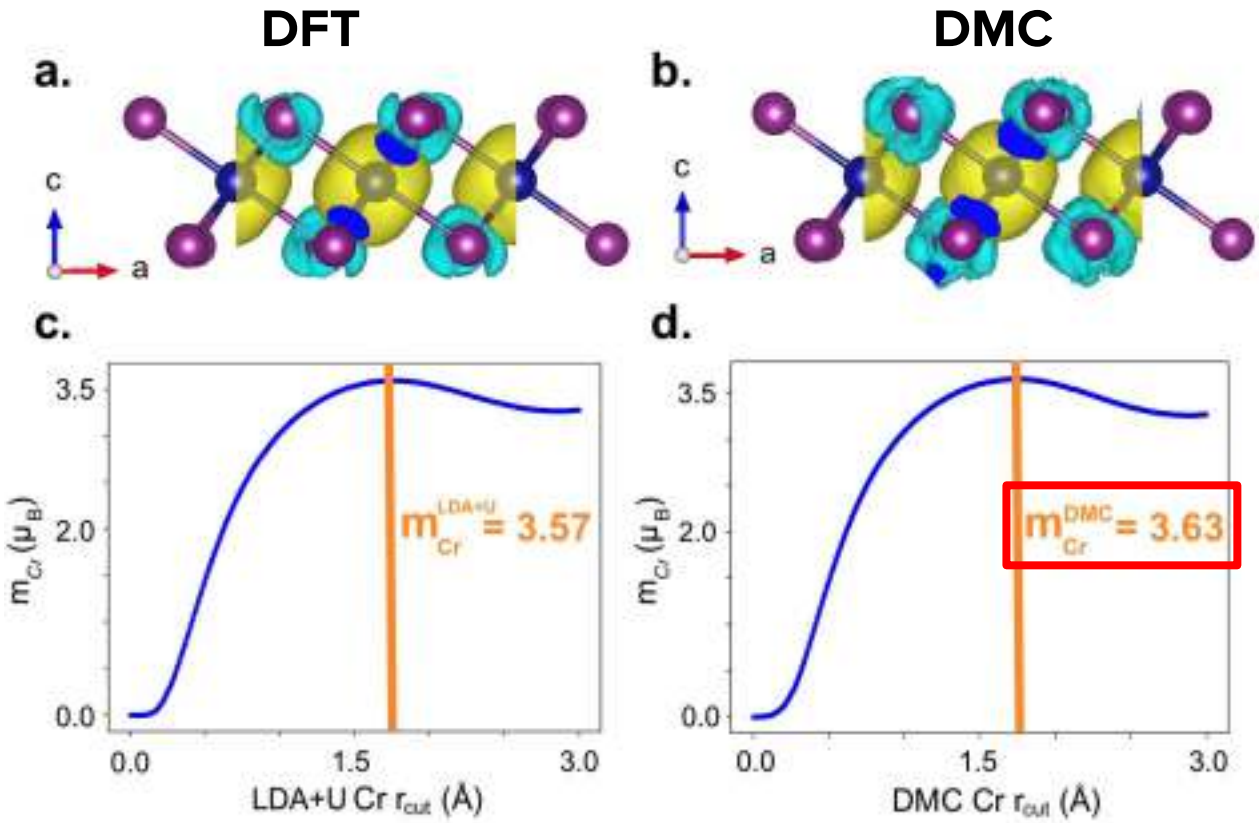

- $a_0$=6.87 Å
- $d_{Cr\text{-}I}$=2.72 Å
- $\theta_1$= 90.4°
- $\theta_2$= 175.4°

| Ref. | Method | $a_0$ (Å) | $m_{Cr}$ ($\mu_B$) | $m_I$ ($\mu_B$) |
|---|---|---|---|---|
| *This work* | LS-DMC | 6.87(3) | 3.61(9) | -0.14(5) |
| *This work* | LDA+$U$ | 6.695 | 3.497 | -0.099 |
| *Li*[32] | GGA+$U$ | 6.84* | 3.28 | – |
| *Yang*[71] | GGA+$U$ | – | 3.32 | – |
| *Wu*[72] | GGA+$U$ | 6.978 | 3.106 | – |
| *Lado*[47] | DFT+$U$ | 6.686 | 3 | – |
| *Zhang*[52] | PBE(HSE06) | 7.008 | 3.103 | – |

<.5% Difference With STM Experiments

*D. Staros, B. Rubenstein, et al., JCP (2022); J. Tiihonen et al., JCP (2021).*

# $CrI_3$'s MAGNETISM: GEOMETRY MATTERS!




- Moments Expected to Be ~3 $\mu_B$
- Moments Found to Be *Substantially Larger*
- Iodine Moments Are Also More Negative
- Note Beyond-Energy Predictions

*(Note: Using DMC-optimized structure.)*

*D. Staros, B. Rubenstein, et al., JCP (2022).*

# SURROGATE METHODS FOR REACTION PATHWAYS

# GENERALIZING SURROGATE METHODS TO TRANSITION STATES AND PATHWAYS

BROWN

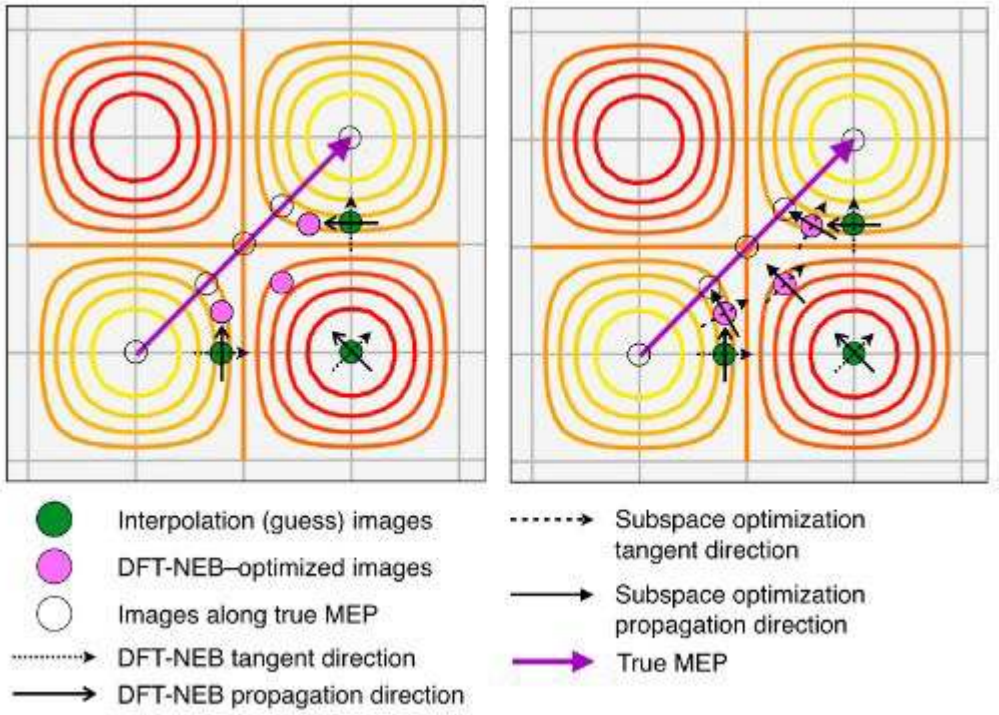
Can generalize to find:

## Transition States

- Search for the minimum along all directions but one

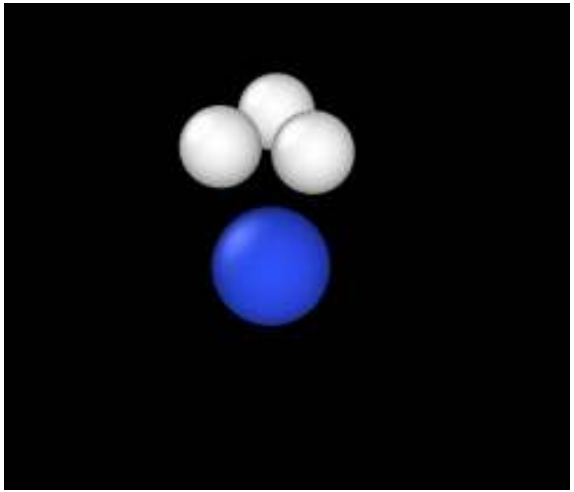
## Minimum Energy Pathways

- Search in a subspace tangent to each point along the path



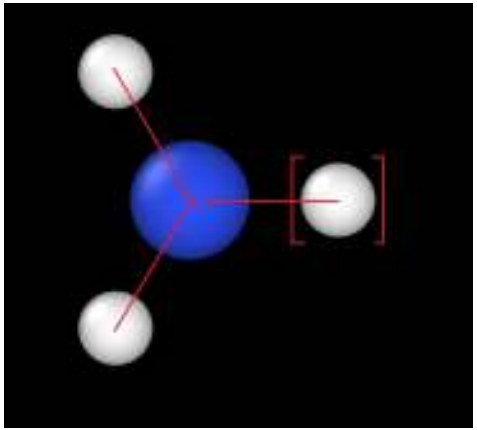
# EXAMPLE 1: AMMONIA INVERSION

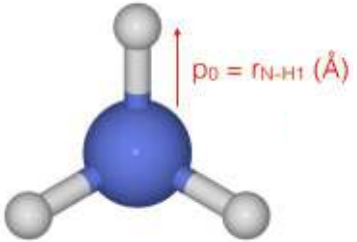
## A Low-Parameter Test Case



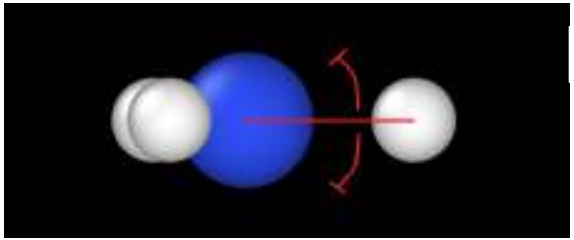
Example of Finding the $NH_3$ Inversion Transition State

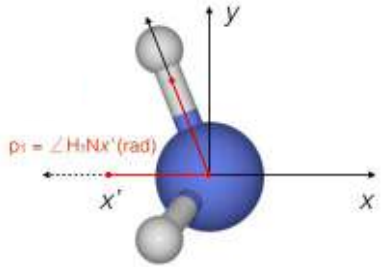
Search Bond Length






Search Angle

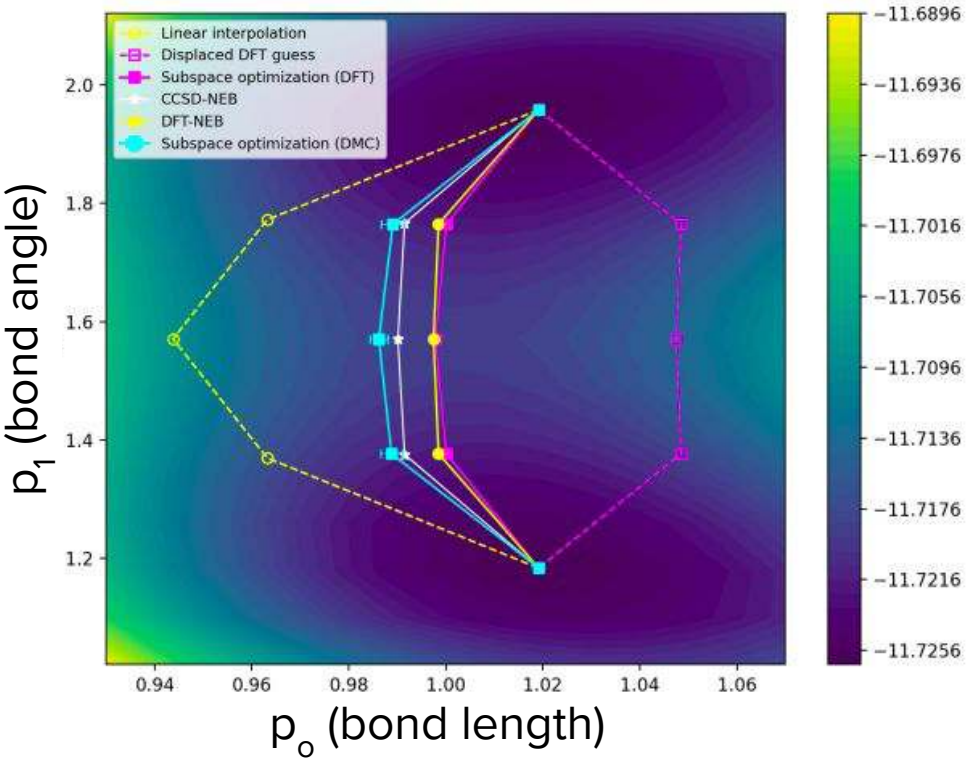




# EXAMPLE 1: AMMONIA INVERSION

BROWN

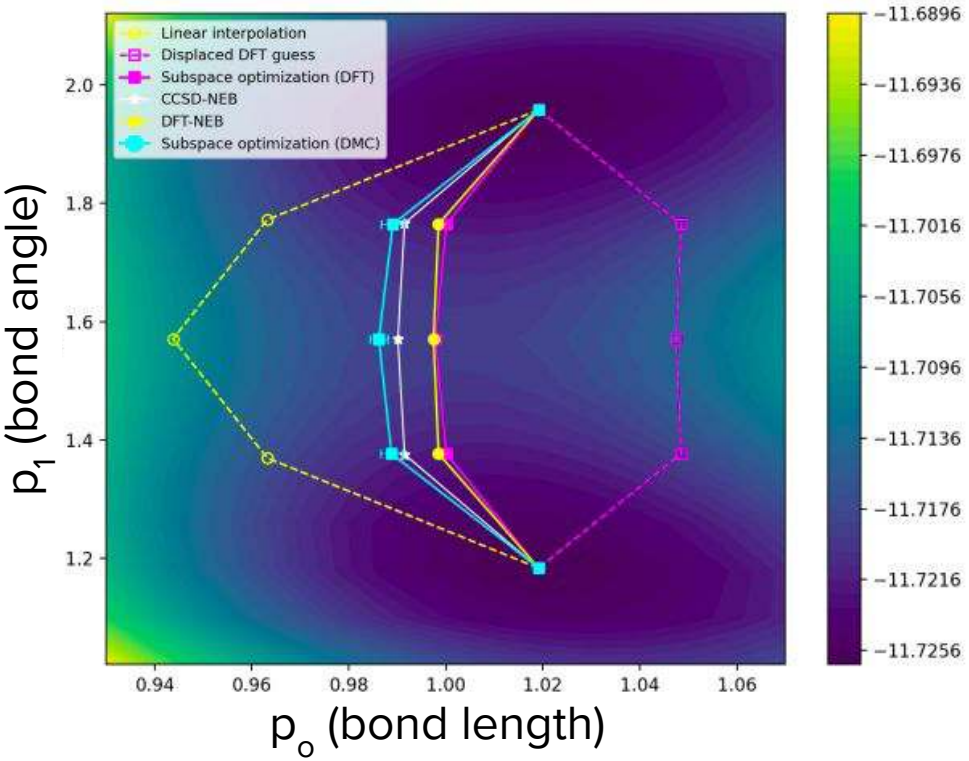
## DMC Minimum Energy Pathway



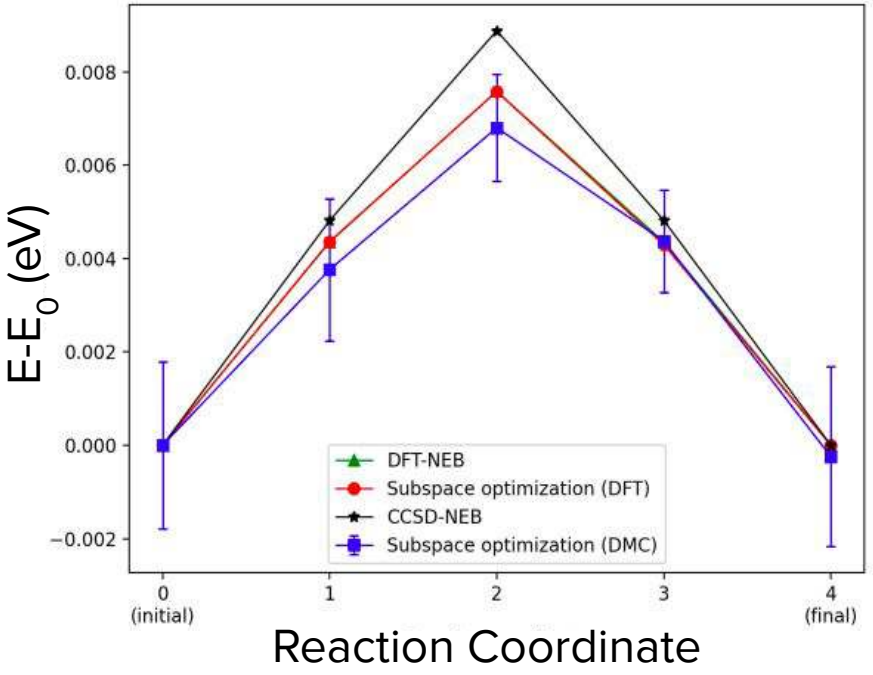
# EXAMPLE 1: AMMONIA INVERSION

BROWN

## DMC Minimum Energy Pathway

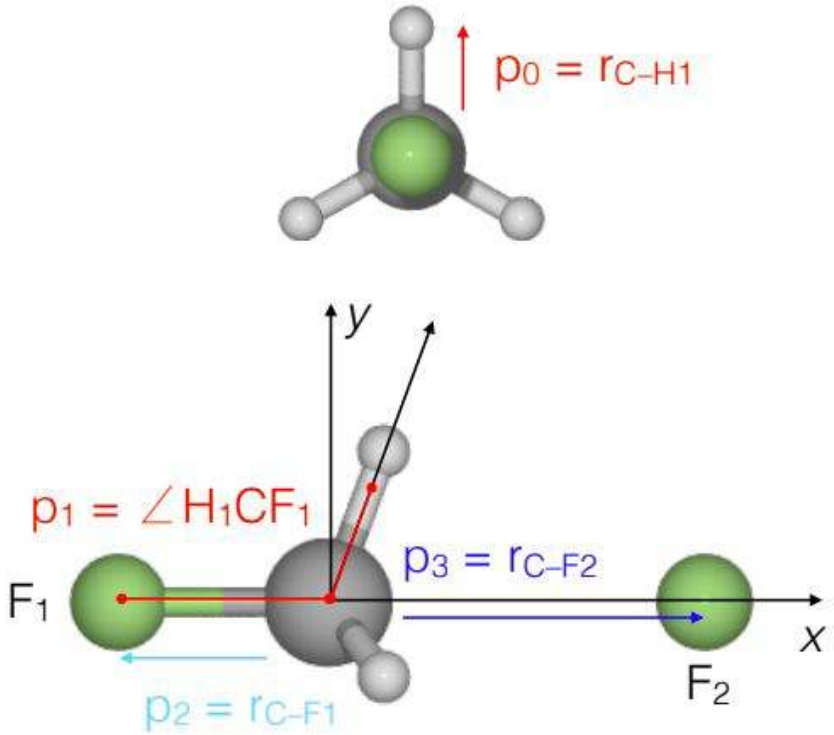



## Energy Differences



# EXAMPLE 2: $S_N2$ REACTION

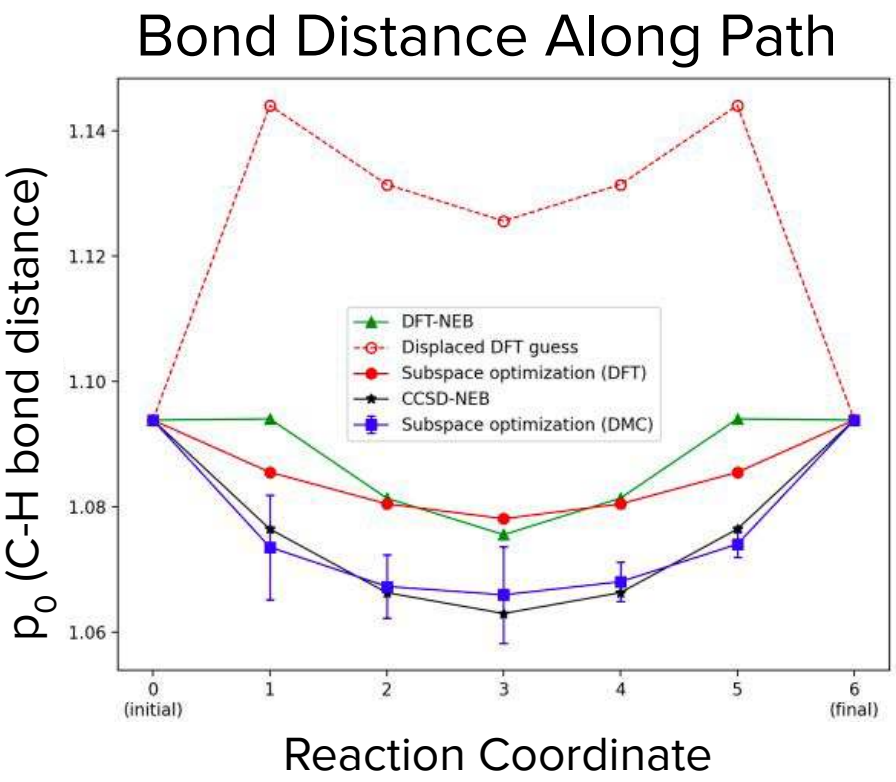
## A Four-Parameter Test Case (with Bond Breaking)




$$F^- + CH_3F \rightarrow FCH_3 + F^-$$

# EXAMPLE 2: $S_N2$ REACTION

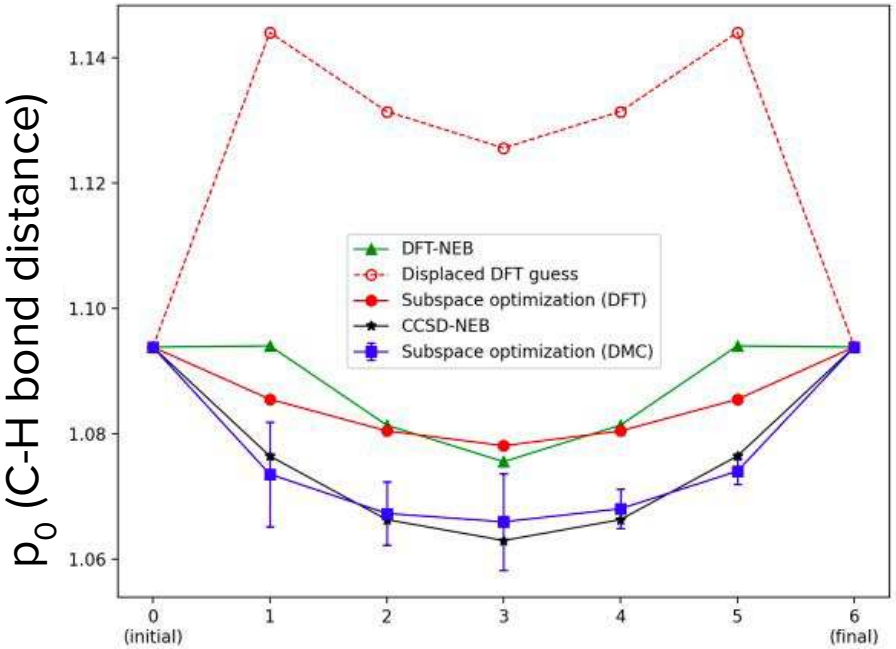
## CCSD-Quality Pathways



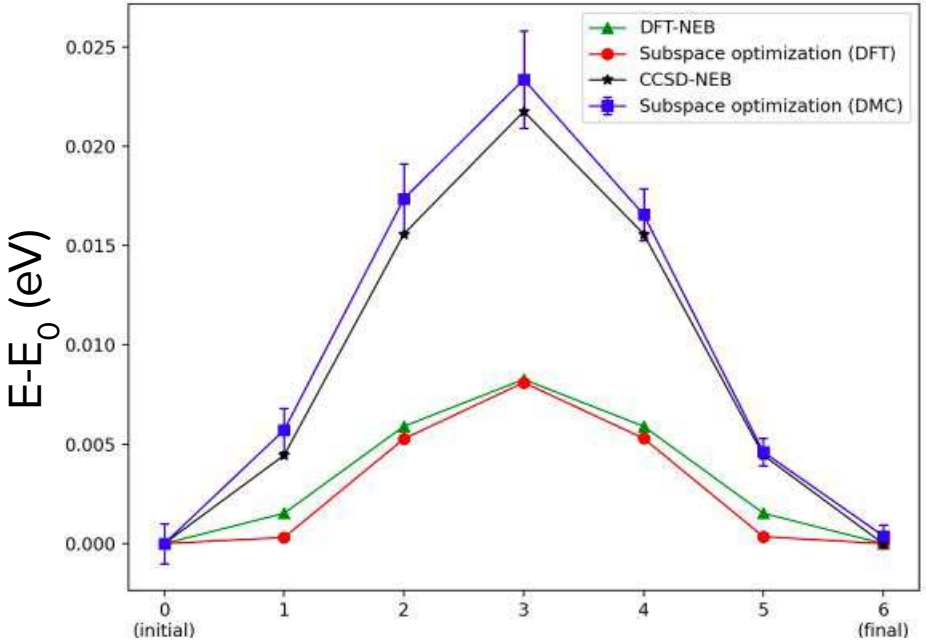
# EXAMPLE 2: $S_N2$ REACTION

## CCSD-Quality Pathways

### Bond Distance Along Path

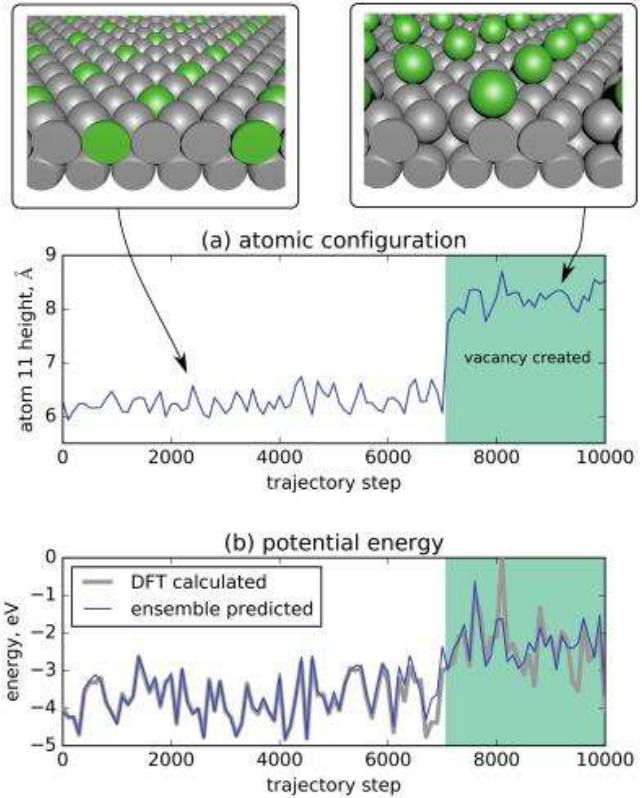



### Energy Differences



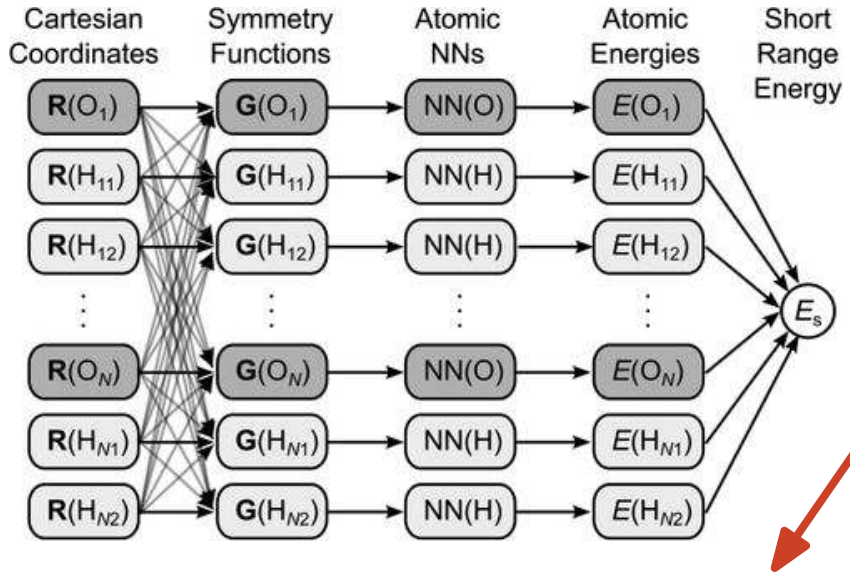
# MACHINE LEARNING FORCES

# LEARNING FORCE FIELDS




Vacancy Formation in fcc(111) Pt via BPNNs

Behler-Parinello Neural Networks (BPNNs)




$$E_S = \sum_{i=1}^{N_{\text{atom}}} E_i$$

$$F_{\alpha,s} = -\frac{\partial E_s}{\partial \alpha} = -\sum_{j=1}^{N_{\text{atom}}} \frac{\partial E_j}{\partial \alpha} = -\sum_{j=1}^{N_{\text{atom}}} \sum_{\mu=1}^{N_{\text{sym},j}} \frac{\partial E_j}{\partial G_{j\mu}} \cdot \frac{\partial G_{j\mu}}{\partial \alpha}$$

*A. Peterson et al., Phys. Chem. Chem. Phys. (2017); J. Behler, Int. J. Quantum Chem. (2015).*

# MOLECULAR CASE STUDIES

## Carbon Dimer, $C_2$

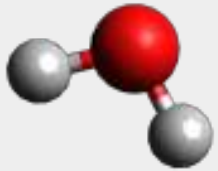
**Coordinates and Training**

- 1 DoF: C-C Bond Distance (R)
- $R=[0.4, 4.0]R_0$, $R_0=1.242$ Å

**Applications**

- NVE, NVT Molecular Dynamics Simulations
- Geometry Relaxation

## Water, $H_2O$



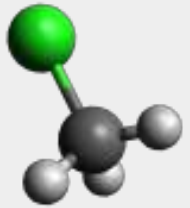
**Coordinates and Training**

- 3 DoFs: 2 O-H Bond Distances (R), H-O-H Bond Angle (Θ)
- $R=[0.5, 2.0]R_0$, $R_0=0.969$ Å
- $\Theta=[0.4, 1.0)\pi$

**Applications**

- NVE, NVT Molecular Dynamics Simulations

## $CH_3Cl$



**Coordinates and Training**

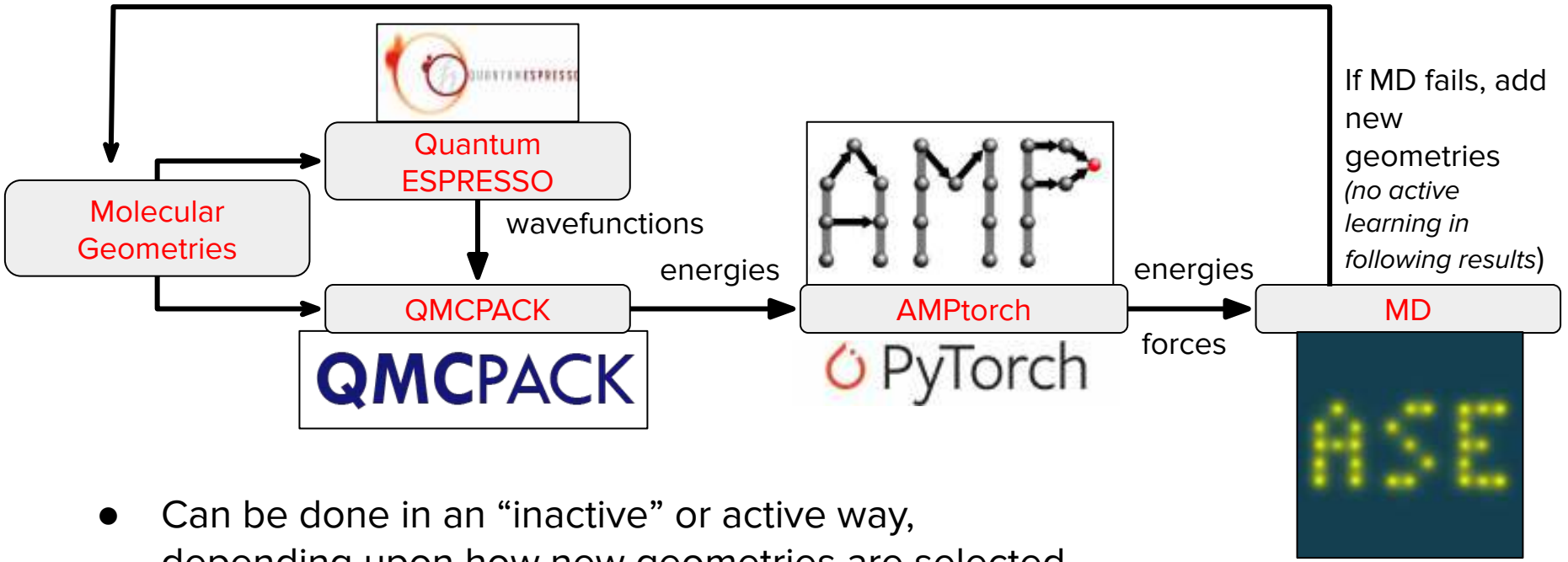
- 9 DoFs: Bond Lengths and Angles
- Adapted from CCSD(T) data set for vibrational spectra[1]

**Applications**

- NVE, NVT Molecular Dynamics Simulations
- Geometry Relaxation

[1] *A. Owens et al., JCP (2015).*

# MACHINE LEARNING WORKFLOW




- Can be done in an “inactive” or active way, depending upon how new geometries are selected

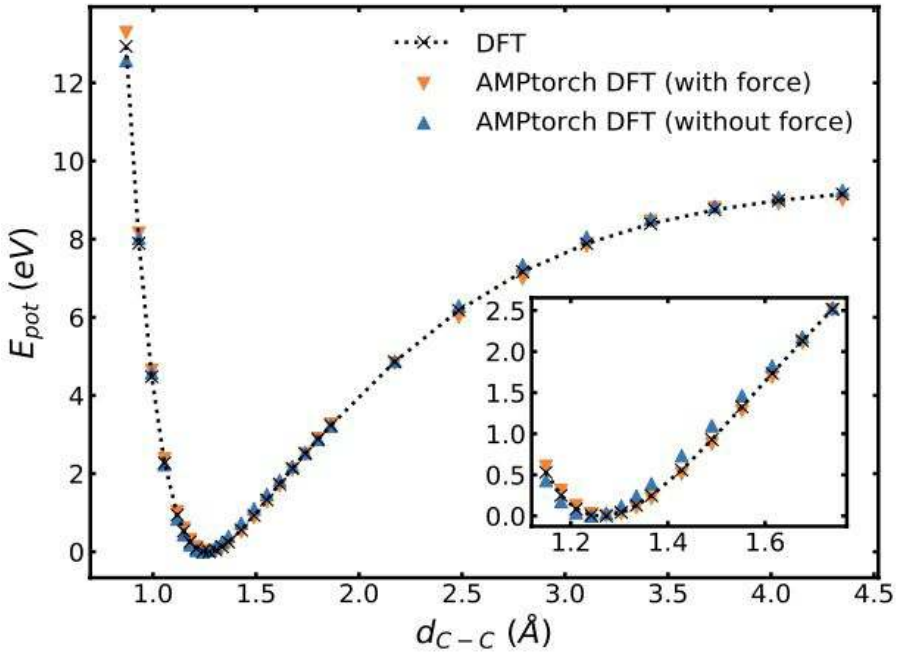
*A. Khorshidi and A. Peterson, Comp. Phys. Comm. (2016), AMPTorch: Ulissi Group at CMU.*

# LEARNING FORCES FROM ENERGIES

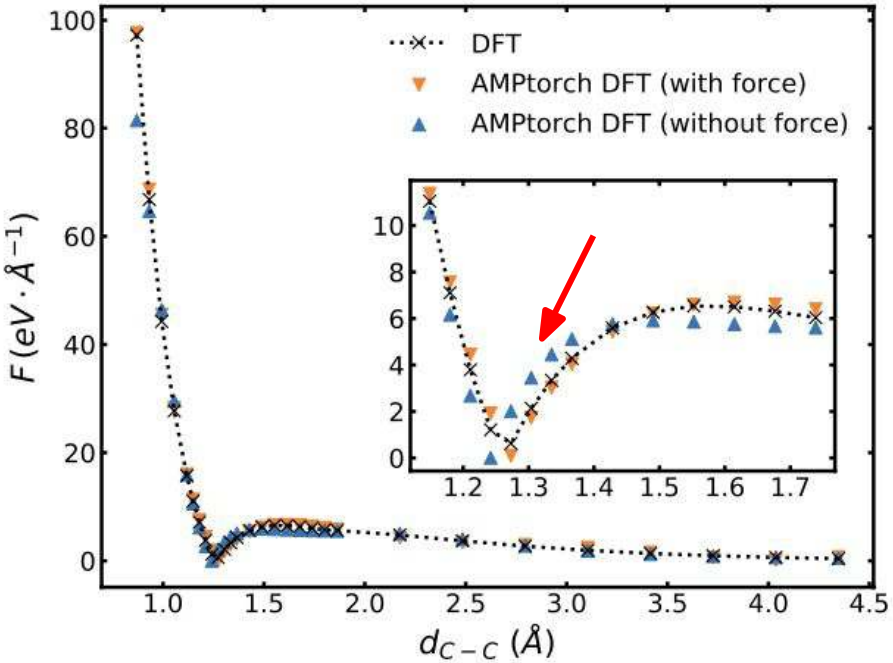
## $C_2$ As a Simple Example with DFT

BROWN

### Energies




### Forces

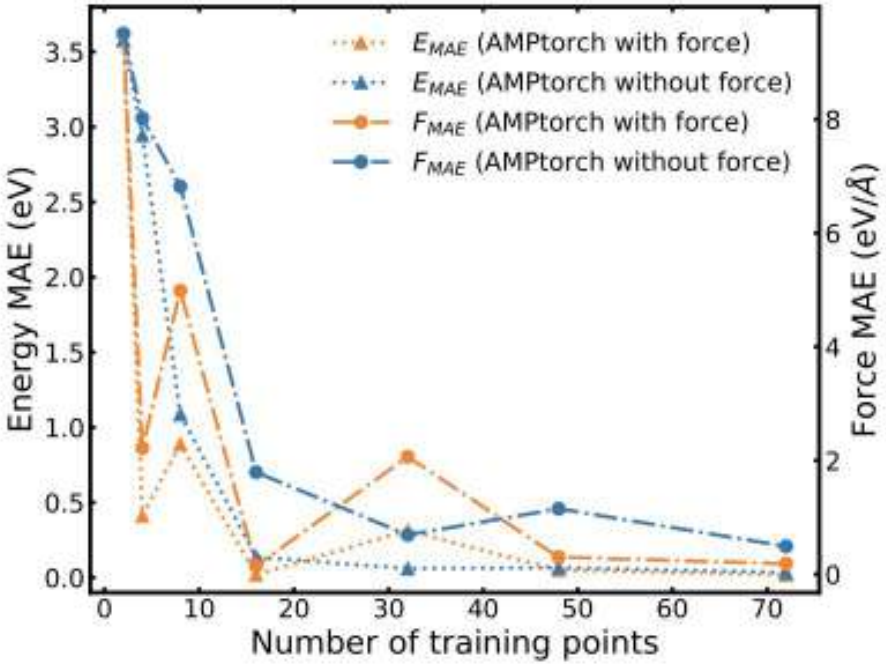



*C. Huang and B. Rubenstein, JPCA (2023).*

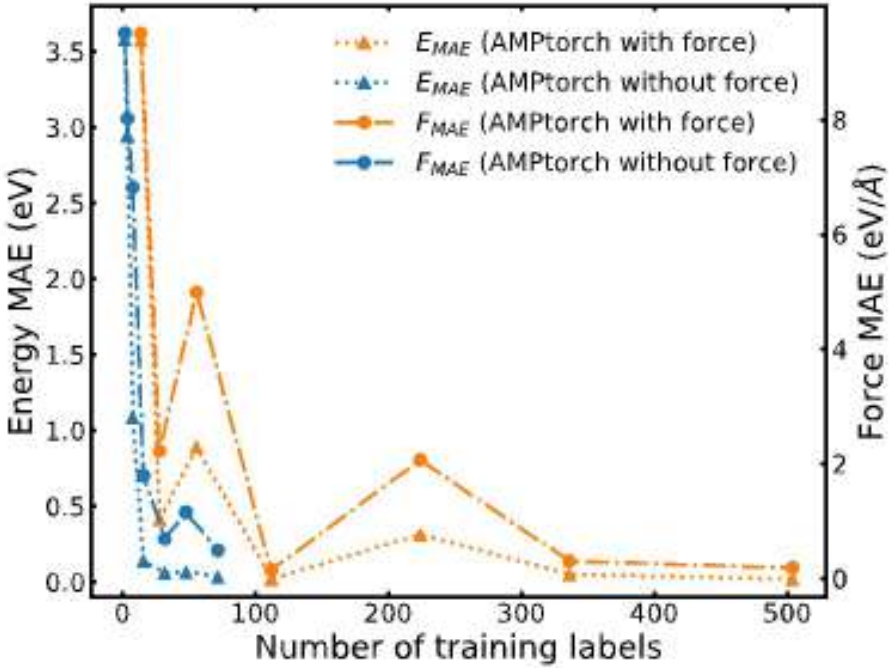
# LEARNING FORCES FROM ENERGIES

## Limits on Errors for $C_2$

### Number of Training Points




### Number of Training Labels



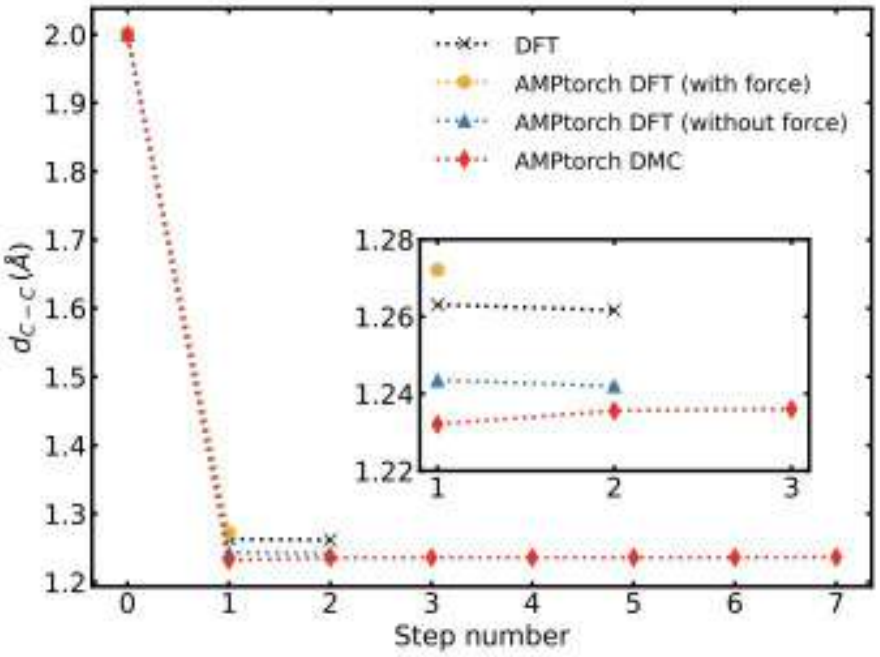

*C. Huang and B. Rubenstein, JPCA (2023).*

# GEOMETRY OPTIMIZATION

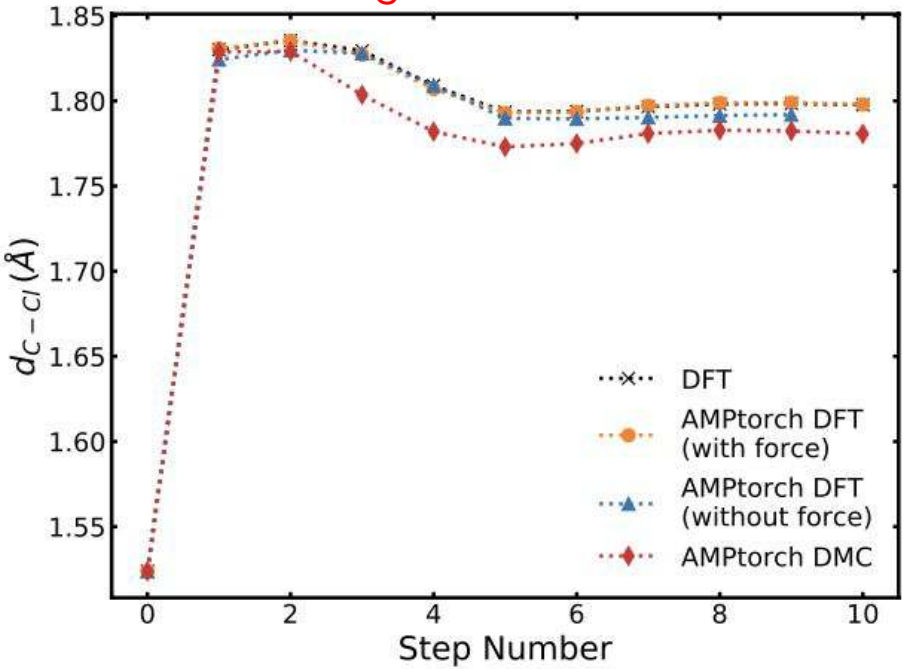
## Relatively Rapid Convergence

BROWN

### $C_2$ (1 dof)



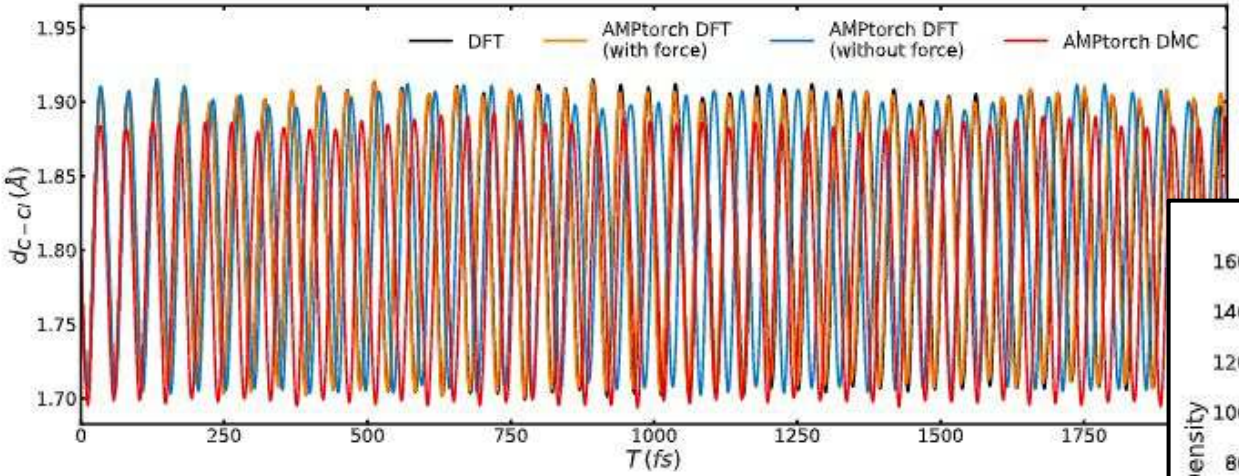

### $CH_3Cl$ (9 dofs)

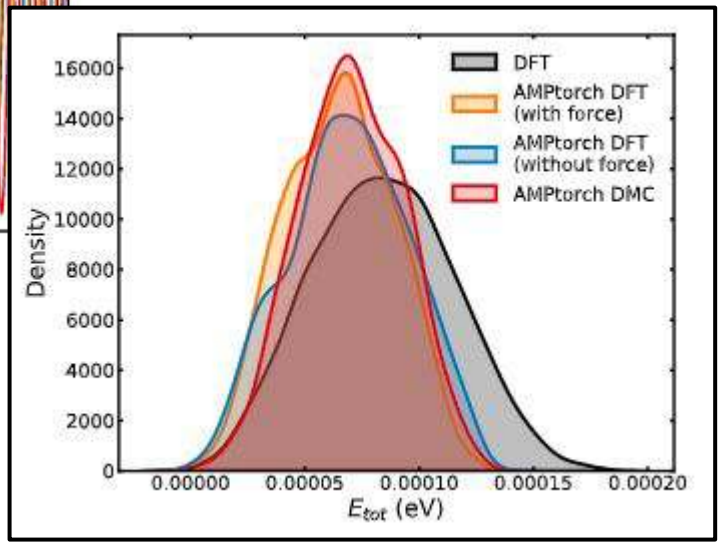



*C. Huang and B. Rubenstein, JPCA (2023).*

# MOLECULAR DYNAMICS

## Reasonable Dynamics for $CH_3Cl$



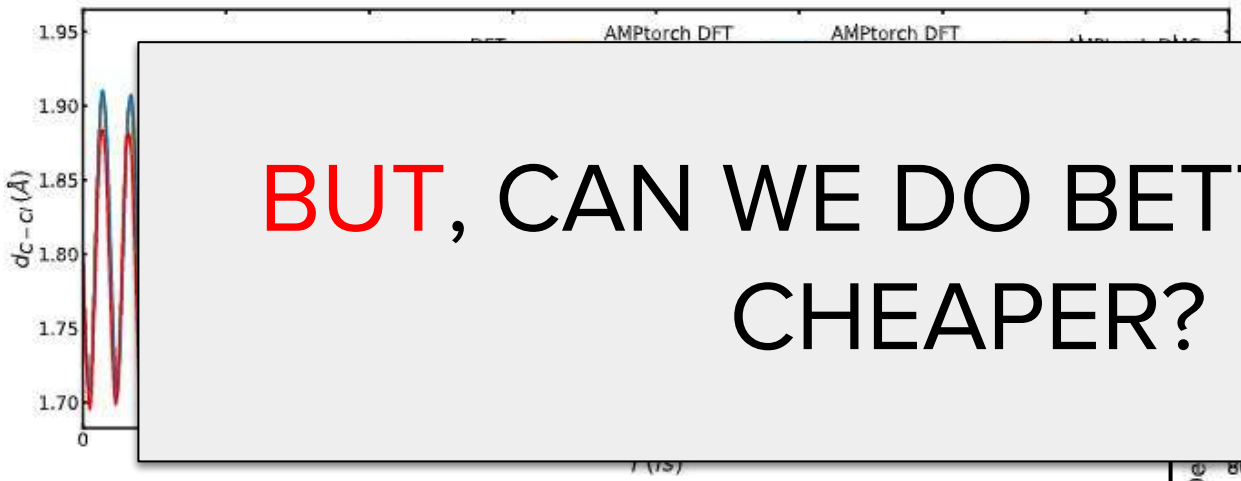

- Relatively close, but not perfect agreement between simulations with and without forces

*C. Huang and B. Rubenstein, JPCA (2023).*

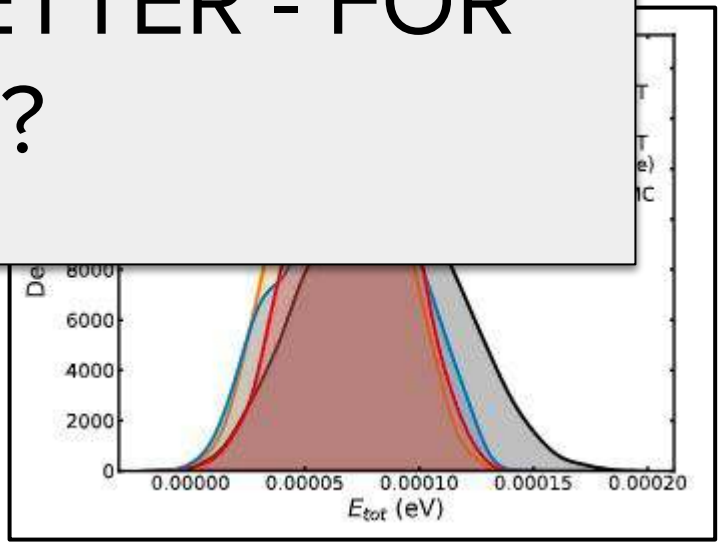
# MOLECULAR DYNAMICS

## Reasonable Dynamics for $CH_3Cl$

BROWN




BUT, CAN WE DO BETTER - FOR CHEAPER?



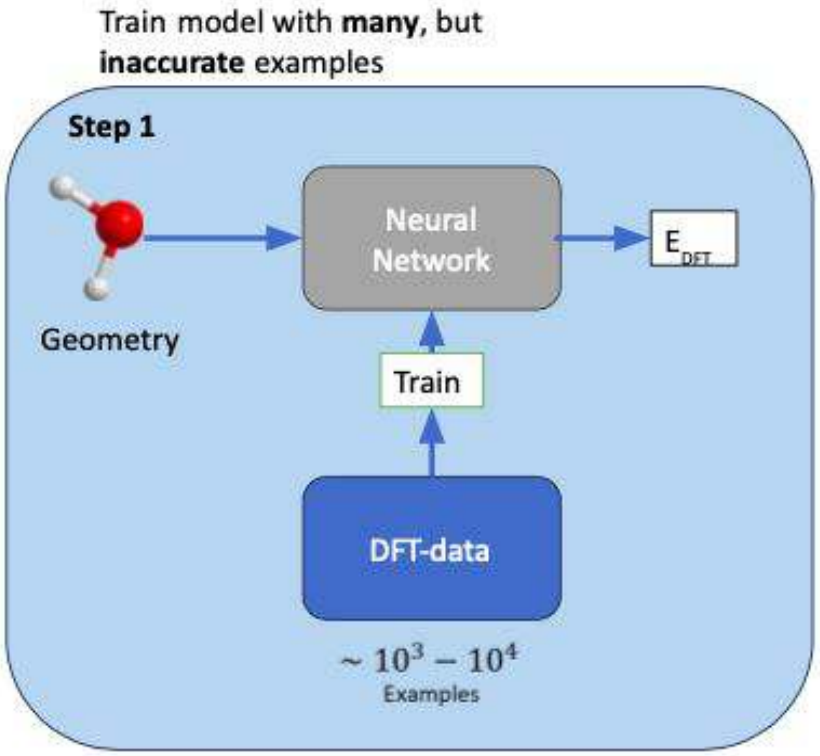

- Relatively close, but not perfect agreement between simulations with and without forces

*C. Huang and B. Rubenstein, JPCA (2023).*

# TRANSFER LEARNING FORCES

# TRANSFER LEARNING

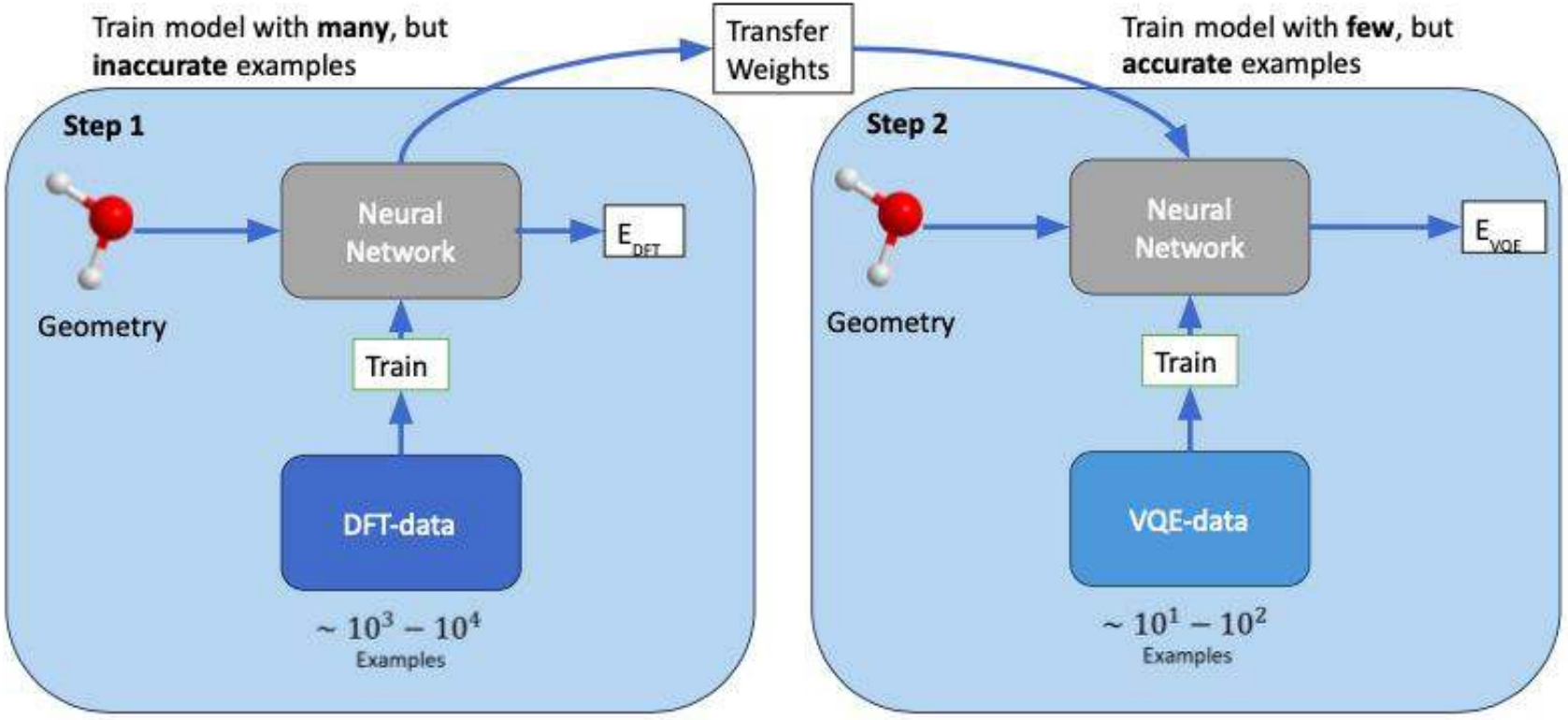
## Learn DFT Baseline, Correct with More Accurate Approaches




*A. Khan et al., To appear (2024); M. Chen et al., JCTC (2023).*

# TRANSFER LEARNING

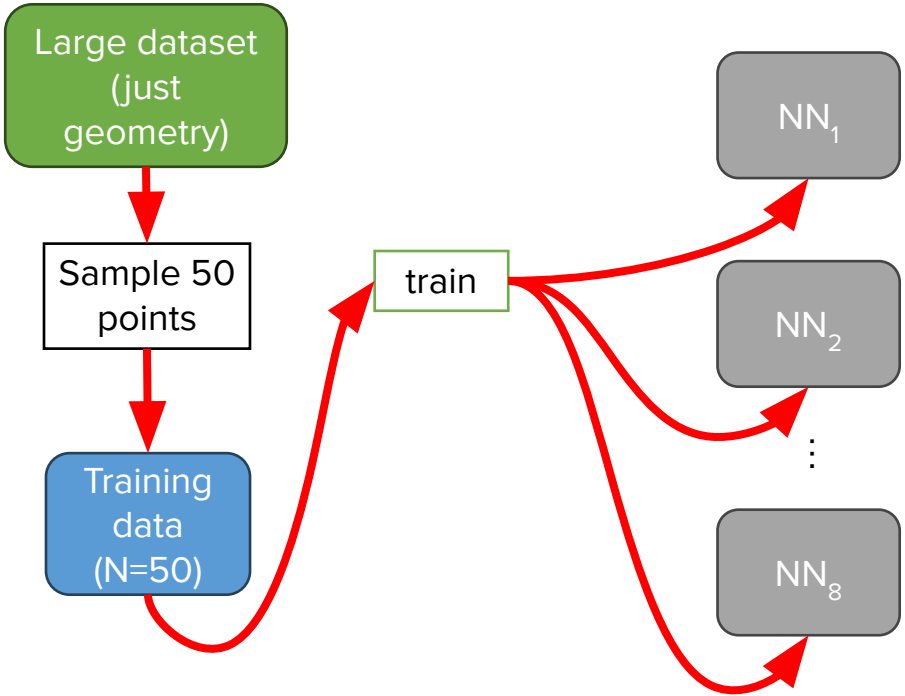
## Learn DFT Baseline, Correct with More Accurate Approaches




*A. Khan et al., To appear (2024); M. Chen et al., JCTC (2023).*

# ACTIVE LEARNING

## Learn DFT Baseline, Correct with Accurate Approaches

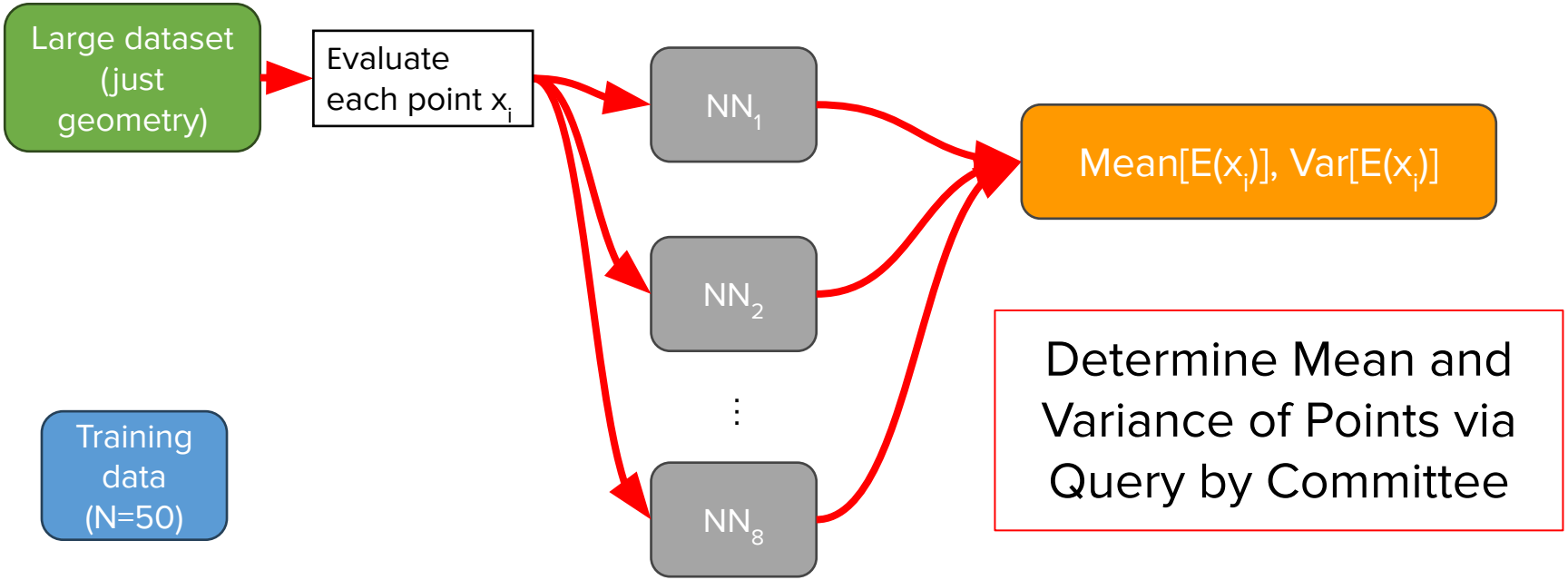



Train energies on initial set of geometries

*A. Khan et al., To appear (2024); M. Chen et al., JCTC (2023).*

# ACTIVE LEARNING

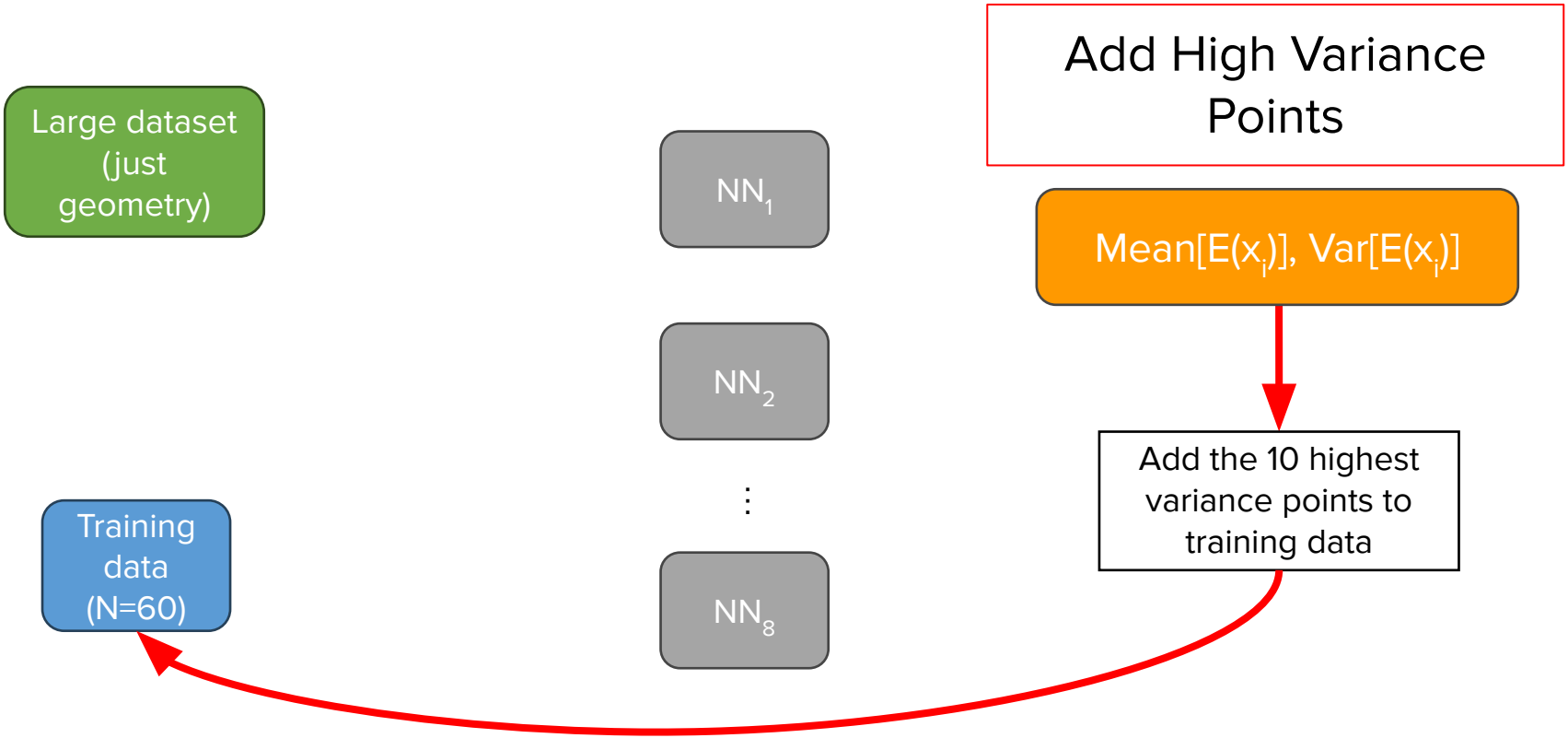
## Learn DFT Baseline, Correct with Accurate Approaches




*A. Khan et al., To appear (2024); M. Chen et al., JCTC (2023).*

# ACTIVE LEARNING

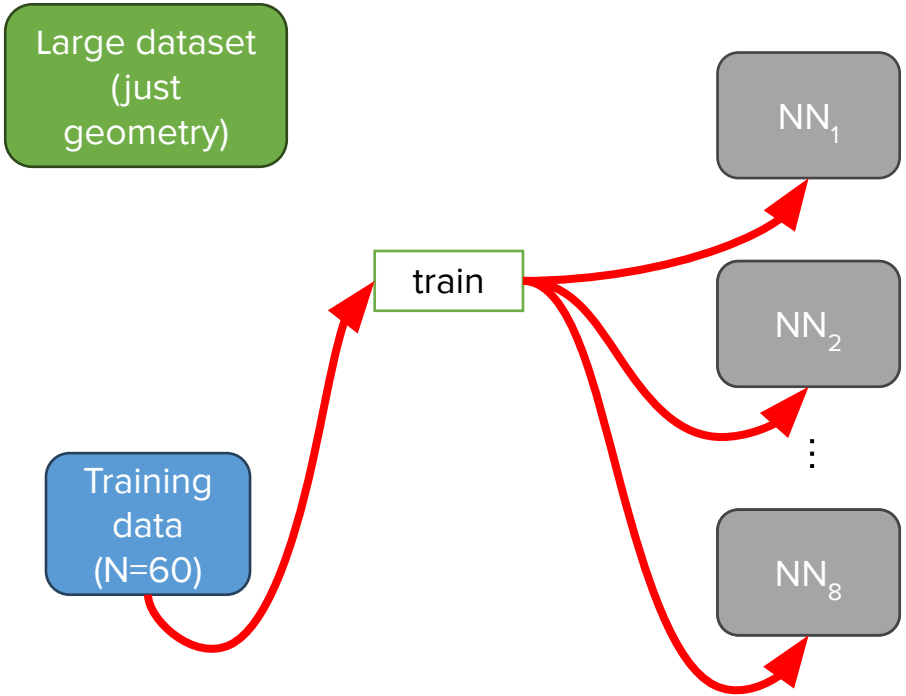
## Learn DFT Baseline, Correct with Accurate Approaches




*A. Khan et al., To appear (2024); M. Chen et al., JCTC (2023).*

# ACTIVE LEARNING

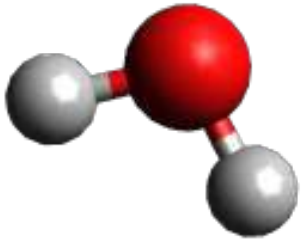
## Learn DFT Baseline, Correct with Accurate Approaches



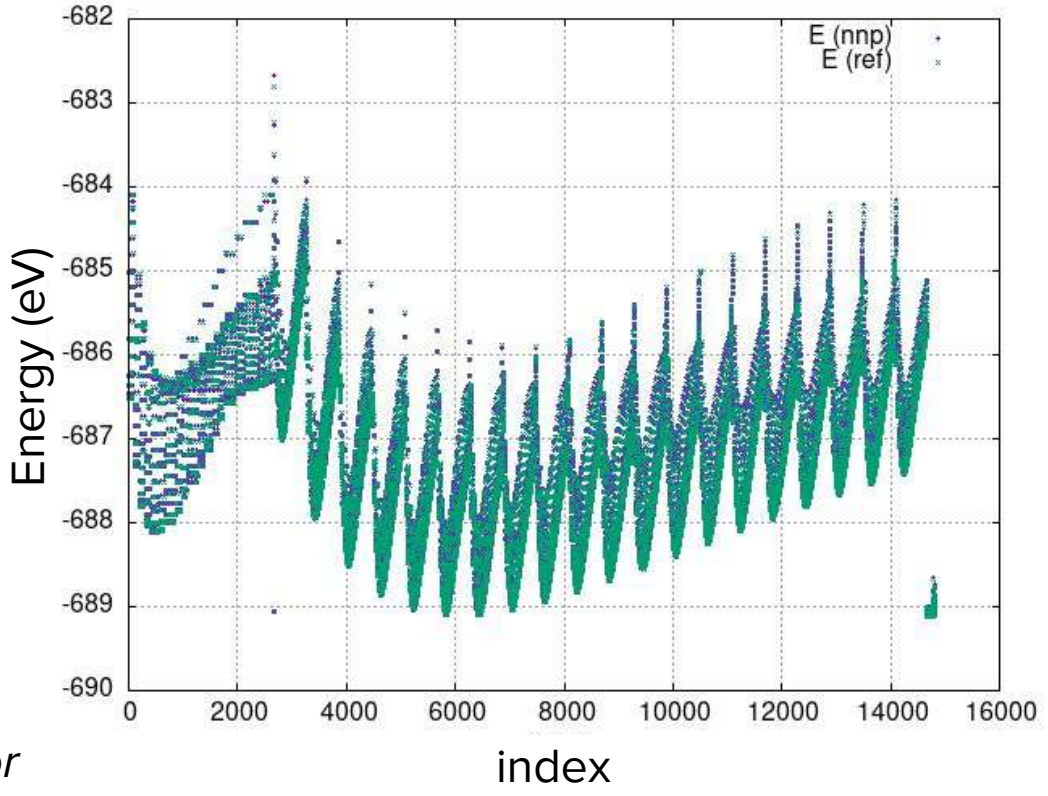

Retrain...
And Iterate

*A. Khan et al., To appear (2024); M. Chen et al., JCTC (2023).*

# TEST CASE: THE WATER MONOMER



- One of the simplest molecular systems with multidimensional potential energy surface (PES)
- ~16,000 configurations sampled using molecular dynamics
- Train on PBE0/STO-6G level of theory; transfer to VQE and FCI (*for now*)



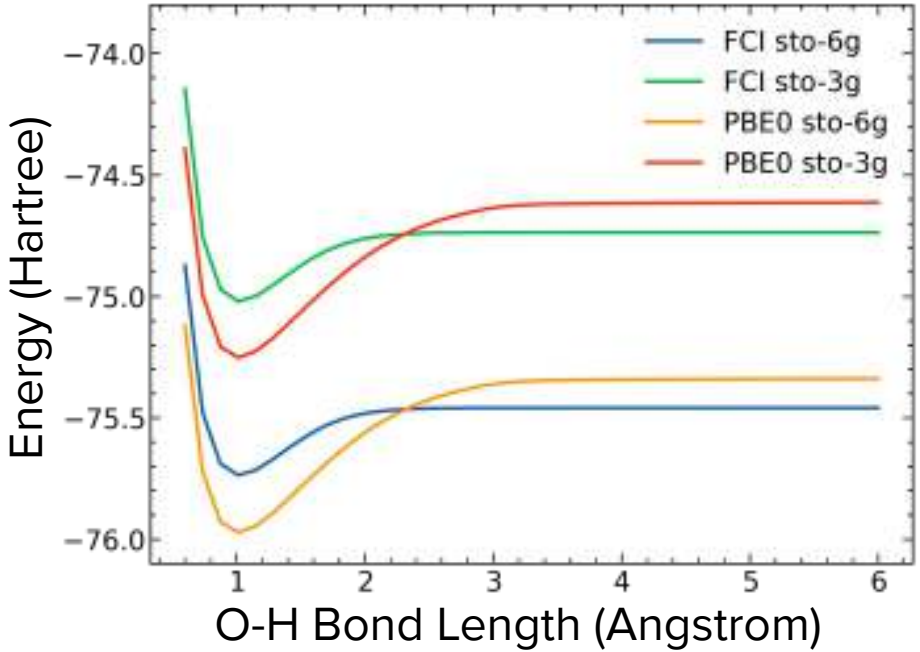

*A. Khan et al., To appear (2024).*

# TEST CASE: THE WATER MONOMER

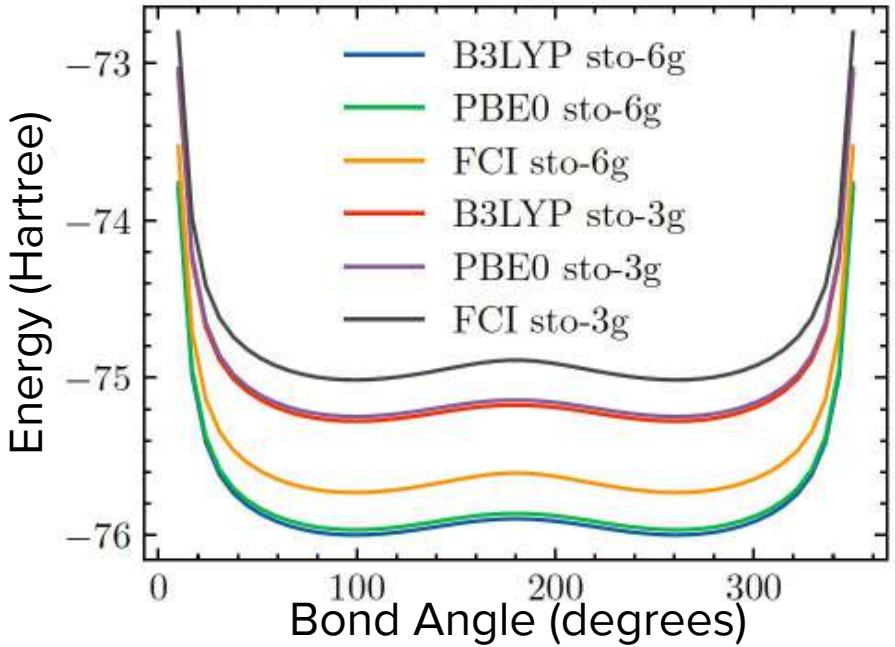
## Comparison of Electronic Structure Results

BROWN

### Bond Lengths



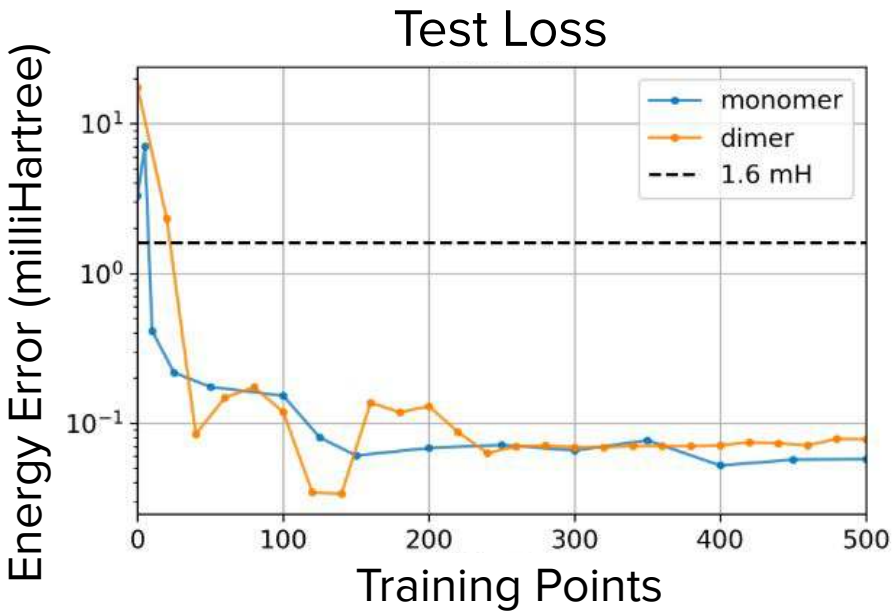

### Bond Angles




*A. Khan et al., To appear (2024).*

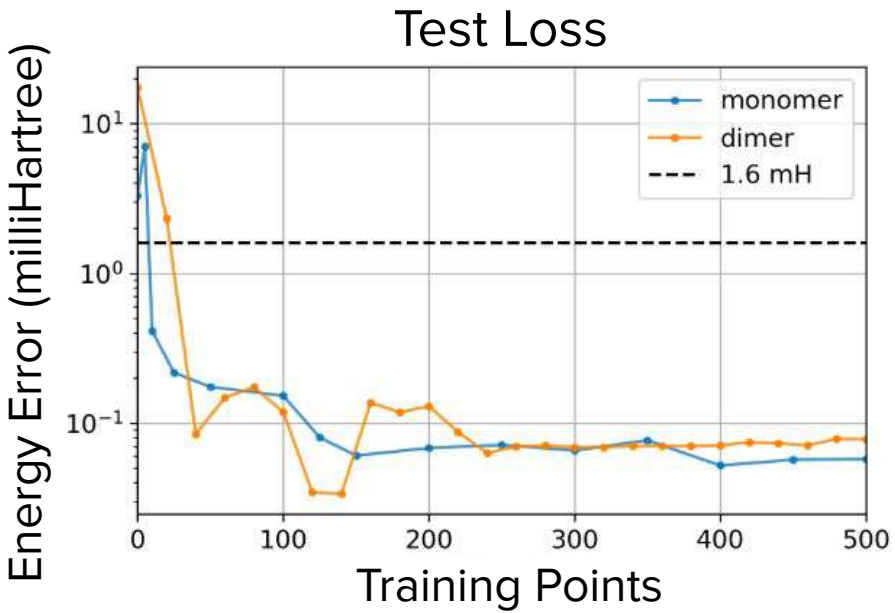
# TEST CASE: THE WATER MONOMER

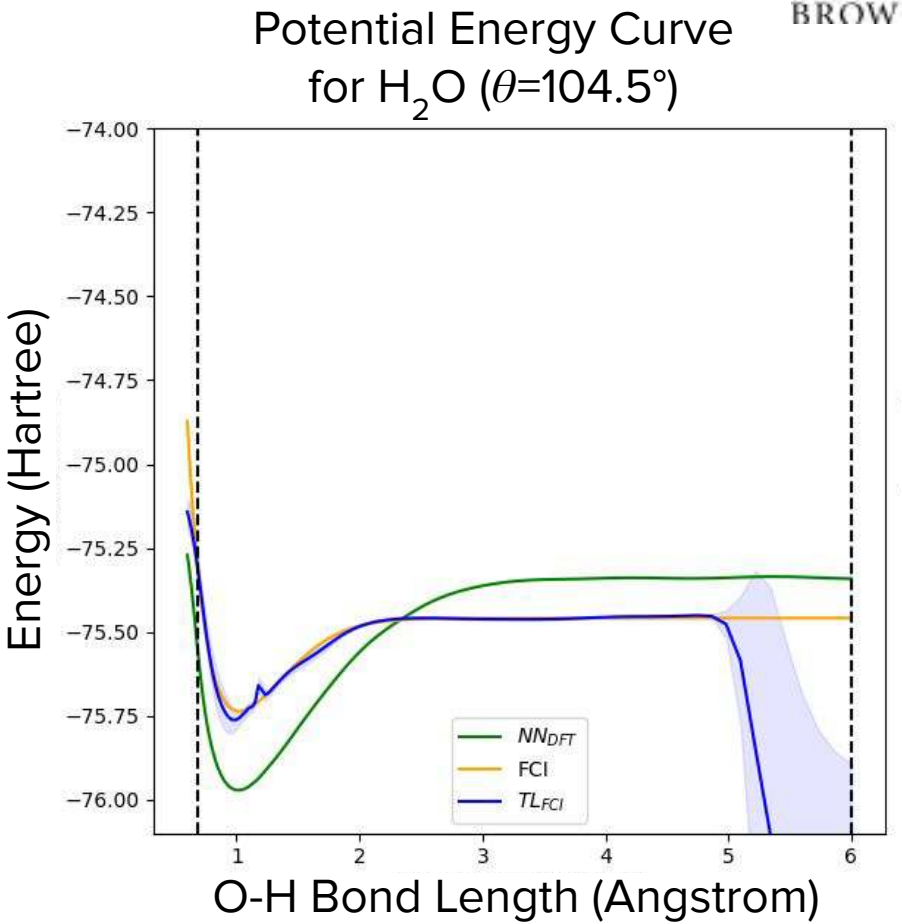
BROWN



# TEST CASE: THE WATER MONOMER

BROWN

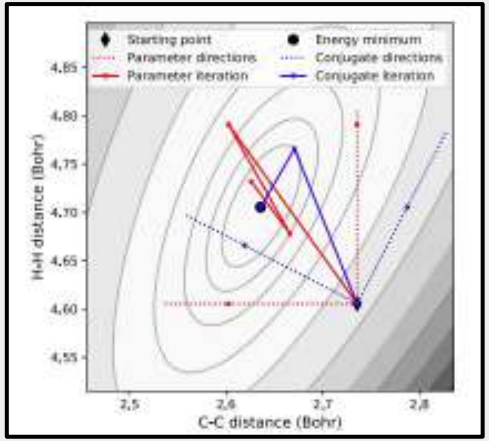


# TODAY'S OUTLINE

## SURROGATE METHODS

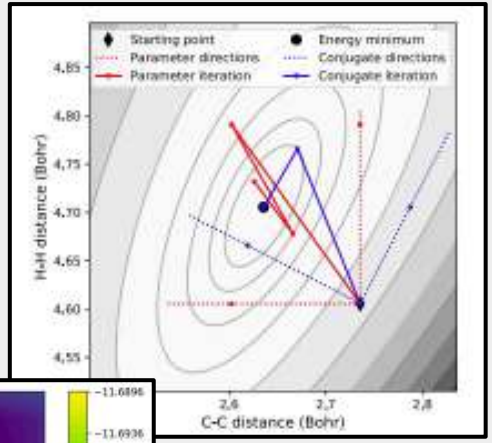
Surrogate
Hessian
Line
Search

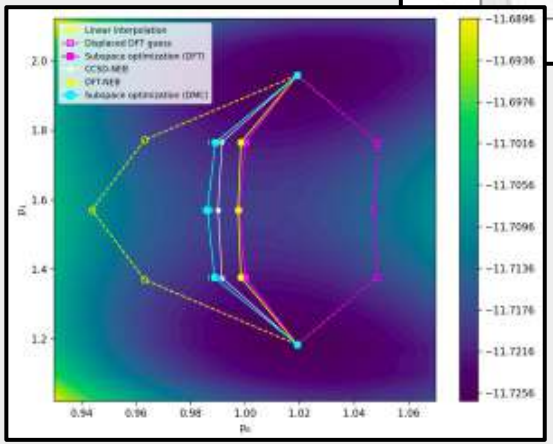


# TODAY'S OUTLINE

## SURROGATE METHODS

Surrogate
Hessian
Line
Search



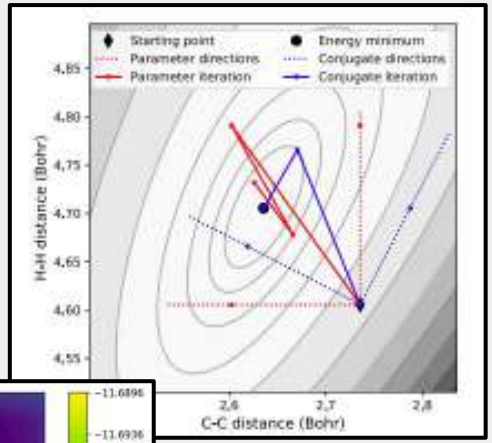



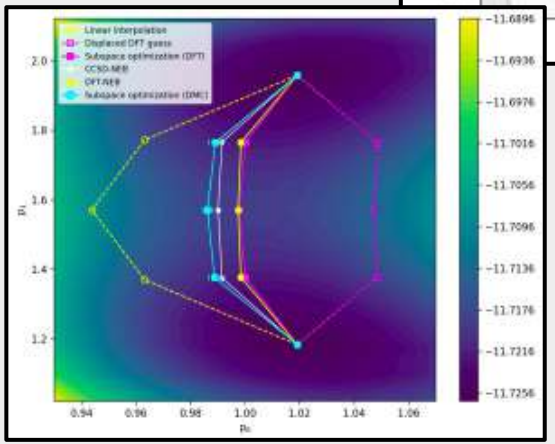
Minimum
Energy
Pathways

# TODAY'S OUTLINE

## SURROGATE METHODS

Surrogate Hessian Line Search

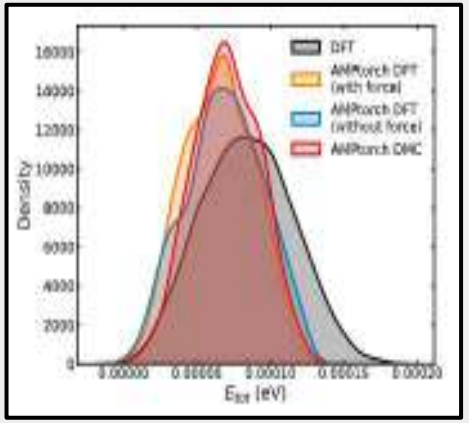


Minimum Energy Pathways

## ML METHODS

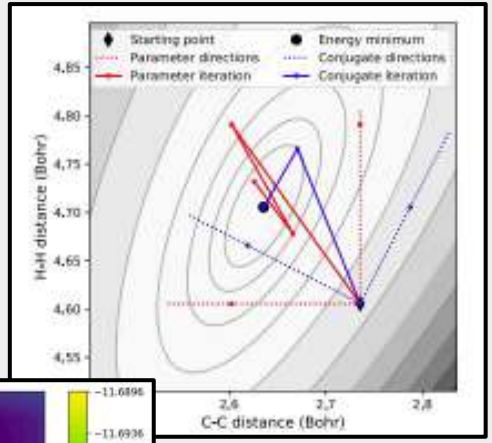
QMC Dynamics with BPNNS

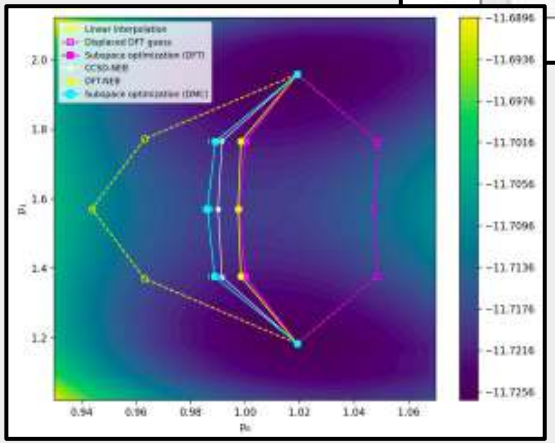


# CONCLUSIONS

## SURROGATE METHODS

Surrogate Hessian Line Search

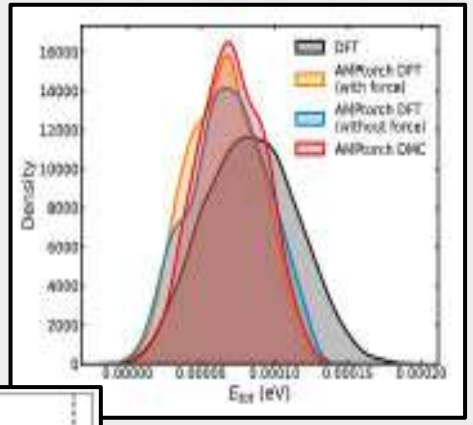


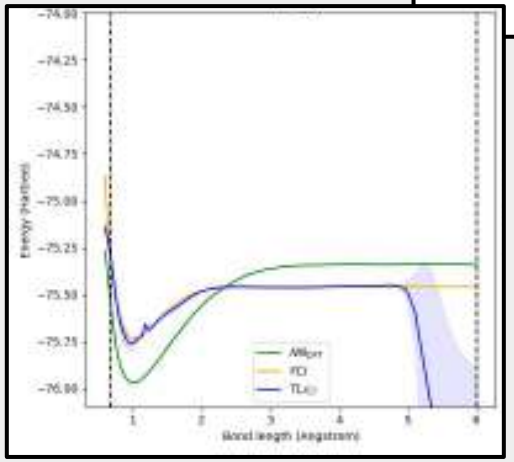



Minimum Energy Pathways

## ML METHODS

QMC Dynamics with BPNNS




Transfer Learning

# GROUP ACKNOWLEDGEMENTS

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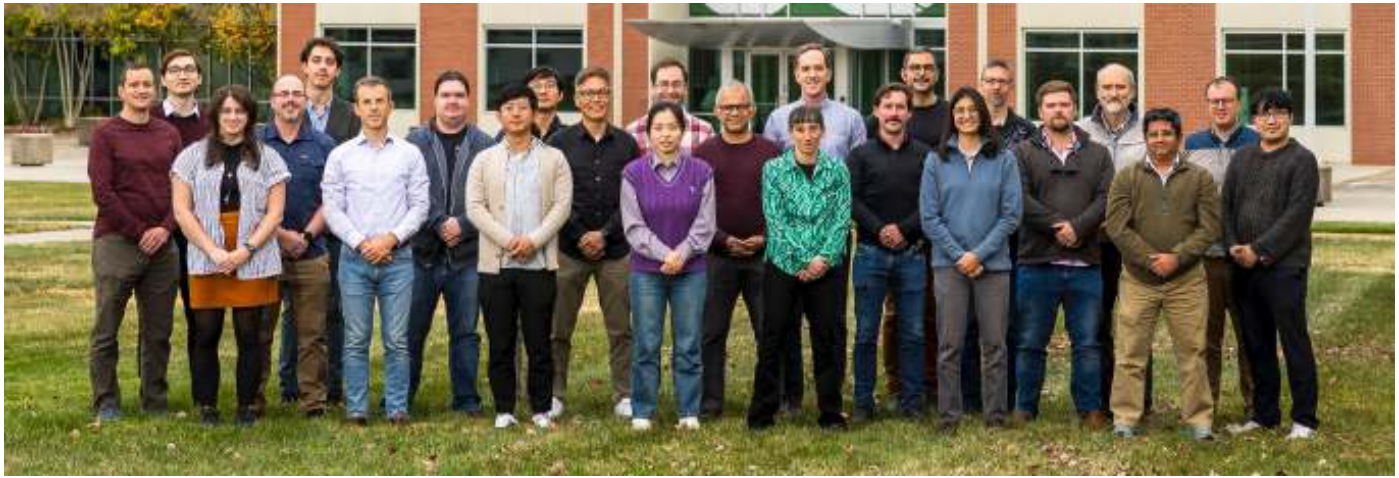
QMCPACK



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Center for the Predictive Simulation of Functional Materials Team, 2023