Minima-preserving neural network (MP-NN) for potential energy surface approximation

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Exascale Catalytic Chemistry

https://ecc-project.sandia.gov/

Accurate adsorbate thermochemistry is essential for microkinetic mechanisms

To calculate equilibrium constants:

$$\frac{k_f}{k_r} = K_{eq} = \exp\left(\frac{-\Delta G^{\circ}_{rxn}(T)}{RT}\right) = \exp\left(\frac{\Delta S^{\circ}_{rxn}(T)}{R}\right)\exp\left(\frac{-\Delta H^{\circ}_{rxn}(T)}{RT}\right)$$

Obtaining the reverse rate constant k_r from k_f and K_{eq} ensures thermodynamic consistency

The free energies cannot be measured experimentally

→Need reliable theoretical methods

→Comes down to evaluating the adsorbate partition function $\boldsymbol{Q_{ads}}$

Helmholtz

$$F_{ads} = -k_B T ln(Q_{ads})$$

Gibbs

$$G_{ads} = F_{ads} - TS_{ads}$$

$$S_{ads} = -k_B ln(Q_{ads}) + k_B T\left(\frac{\partial ln(Q_{ads})}{\partial T}\right)$$

$$dH_{ads} = k_B T^2\left(\frac{\partial ln(Q_{ads})}{\partial T}\right)$$

$$C_{p,ads} = k_B T^2\left(\frac{\partial^2 ln(Q_{ads})}{\partial T^2}\right) + 2k_B T\left(\frac{\partial ln(Q_{ads})}{\partial T}\right)$$

Slide from Katrin Blondal

A phase space integration approach captures mode coupling and anharmonicity

Inspired by another project[1] in the Goldsmith group
-implementing VRC-TST for barrierless gas-phase reactions[2].

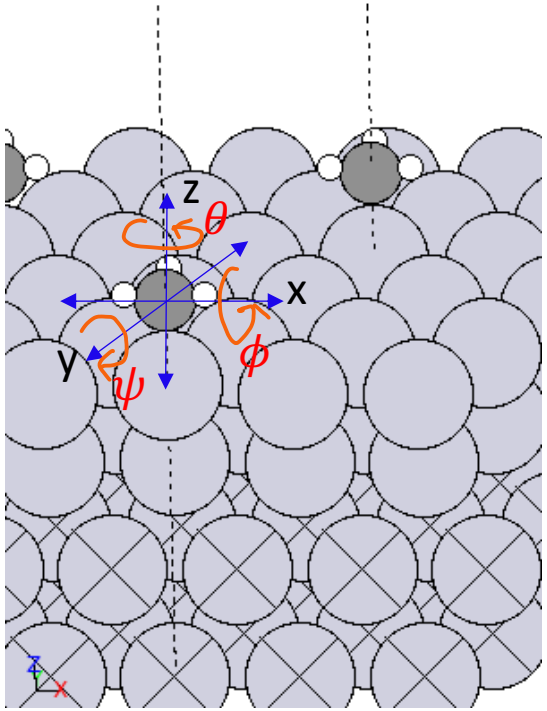
According to classical phase space theory:

$$Q_{class} \sim \int \dots \int \exp\left(-\beta H(p,q)\right) dpdq$$

For a non-linear adsorbate:

$$Q_{6D} = \frac{kinetic\ factor}{h^6} \int_{6D} \exp(-\beta E(q))\, dxdydzd\theta d\phi d\psi$$

$$Q_{ads} = Q_{6D} \prod_{i}^{3N-6} Q_i^{H.O.}$$



[1]X. Chen. (2019). *PhD thesis*, Brown University

[2]S. J. Klippenstein. (1992). *J. Chem. Phys.*, *92*, 367-371

Partition function calculated via phase space integration

- Choose random configurations within a uniformly sampled domain

$$\int_{\Omega} \exp(-\beta E(\boldsymbol{x}))\, dx \approx \frac{\Omega}{M} \sum_{i=1}^{M} \exp(-\beta E(\boldsymbol{x}))$$

- Computationally extremely intensive
  - Monte-Carlo requires large *M* for reasonable accuracy
  - Can require over M = 10,000 to 100,000 configurations (i.e. DFT calculations)
- Solution: replace energy $E(\boldsymbol{x})$ with a pre-constructed surrogate $E_s(\boldsymbol{x})$
  - Given a feasible number of configurations, built an approximation $E(\boldsymbol{x}) \approx E_s(\boldsymbol{x})$
  - Use the surrogate in the Monte-Carlo integral
  - Can afford large *M*, if the surrogate is cheap

$$\int_{\Omega} \exp(-\beta E(\boldsymbol{x}))\, dx \approx \frac{\Omega}{M} \sum_{i=1}^{M} \exp(-\beta E_s(\boldsymbol{x}))$$

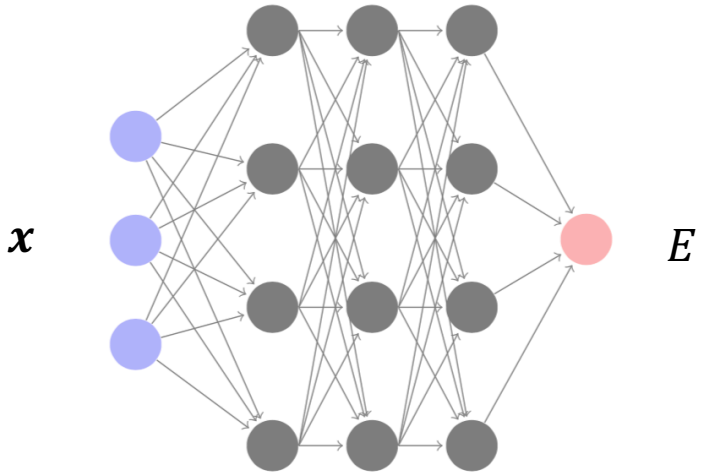
Surrogate construction is a supervised Machine Learning problem

$$E(\boldsymbol{x}) \approx E_s(\boldsymbol{x})$$

Given a set of *training* configurations $(\boldsymbol{x_1}, E(\boldsymbol{x_1})), (\boldsymbol{x_2}, E(\boldsymbol{x_2})), \ldots, (\boldsymbol{x_N}, E(\boldsymbol{x_N}))$

Find a (parametrized) form; i.e. optimize for $\boldsymbol{w}$ $E(\boldsymbol{x}) \approx E_s(\boldsymbol{x}; \boldsymbol{w})$

e.g.
- Polynomial expansion
- Gaussian process
- Neural network (NN)



MP-NN: Approximation of PES should focus on accuracy near minima (if the goal is partition function evaluation)

Small errors near minima in energy $E(\boldsymbol{x}) \approx E_s(\boldsymbol{x})$

can lead to large errors in partition function integrand $e^{-E(\boldsymbol{x})/(kT)} \approx e^{-E_s(\boldsymbol{x})/(kT)}$

- General flexible form (NN or otherwise) surrogate does not preserve the minima information
- We employ handcrafted surrogate form inspired by the quadratic approximation near the PES minimum
- In the case of a single minimum with known Hessian $H(\boldsymbol{x}_0)$:

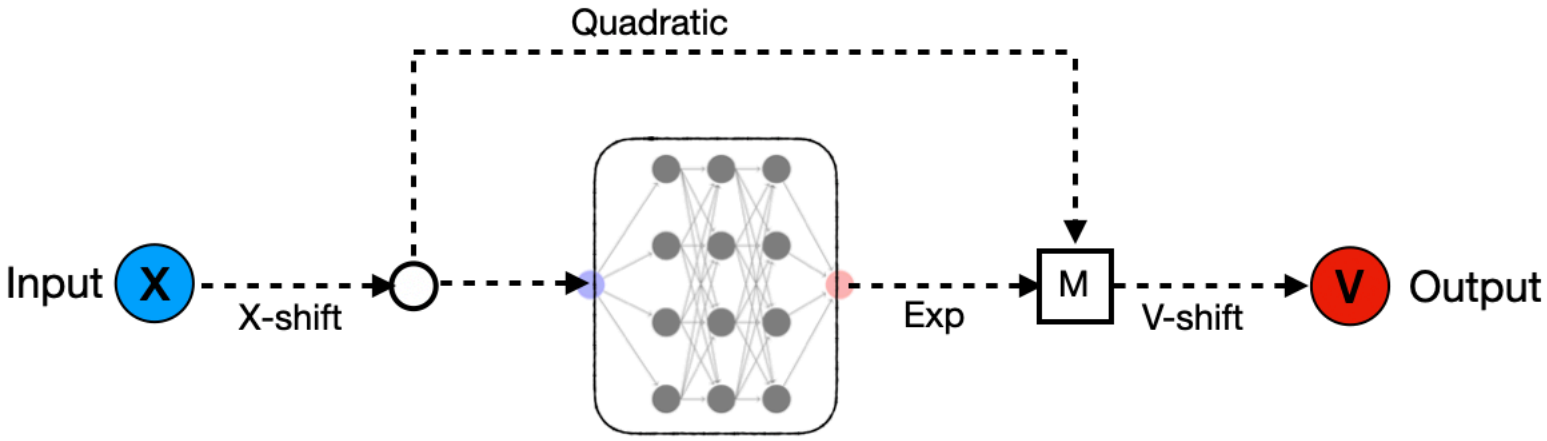
NN serves as a multiplicative correction to a quadratic

$$E_s(\boldsymbol{x}) = E(\boldsymbol{x}_0) + \frac{1}{2}(\boldsymbol{x} - \boldsymbol{x}_0)^T H(\boldsymbol{x}_0)(\boldsymbol{x} - \boldsymbol{x}_0) e^{NN(\boldsymbol{x}-\boldsymbol{x}_0)}$$

MP-NN: Special NN architecture that is accurate near minima by construction

$$E_s(\boldsymbol{x}) = E(\boldsymbol{x}_0) + \frac{1}{2}(\boldsymbol{x} - \boldsymbol{x}_0)^T H(\boldsymbol{x}_0)(\boldsymbol{x} - \boldsymbol{x}_0) e^{NN(\boldsymbol{x} - \boldsymbol{x}_0)}$$

NN serves as a multiplicative correction to a quadratic



MP-NN: Multiple minima case is handled by distance-based linear combination

- Define weights according to distances from minima

$$w_1(x) = e^{-\frac{||\boldsymbol{x}-\boldsymbol{x}_1||}{\epsilon}}$$

$$w_2(x) = e^{-\frac{||\boldsymbol{x}-\boldsymbol{x}_2||}{\epsilon}}$$

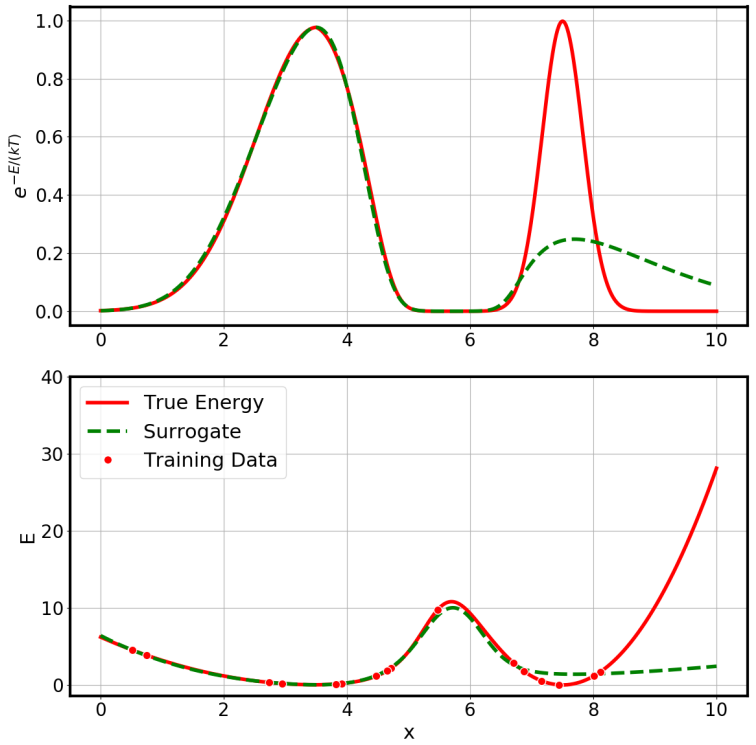
ϵ is a smoothing factor

- Linear combination of energy surrogates, each doing well near one minimum

$$E_s(x) = \frac{w_1(x)E_1(x) + w_2(x)E_2(x)}{w_1(x) + w_2(x)}$$

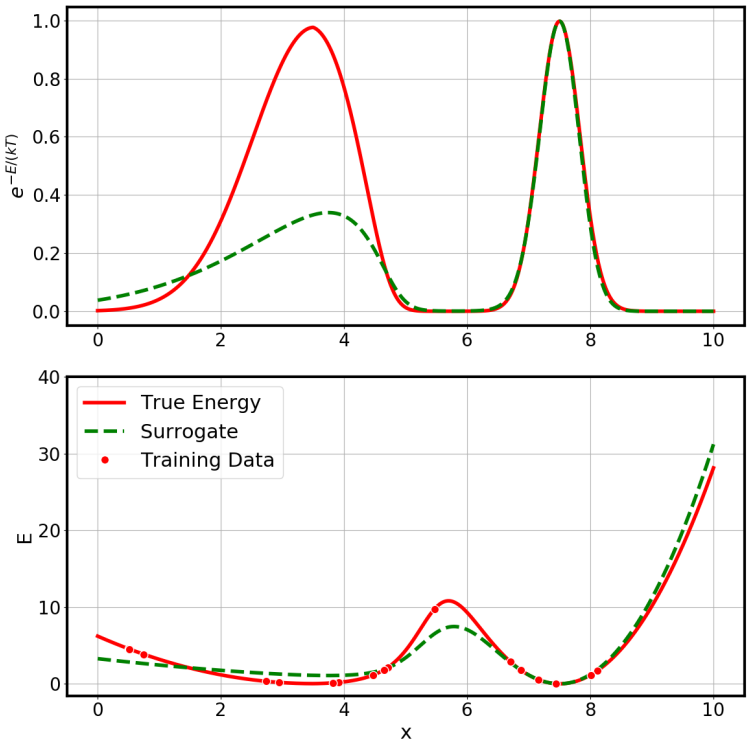
MP-NN: linear combination demo

$$E_s(x) = E_1(x)$$



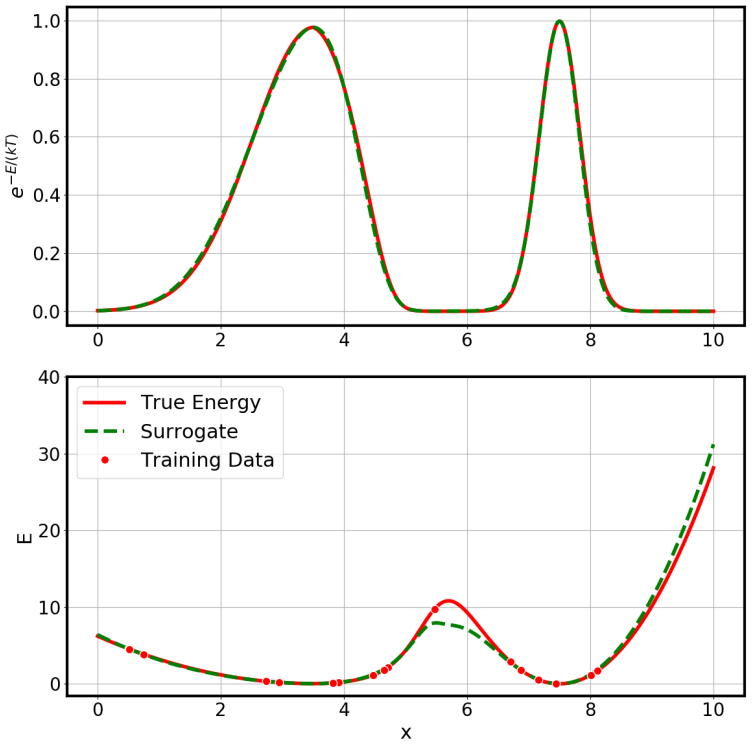
Accurate near the left minimum

$$E_s(x) = E_2(x)$$



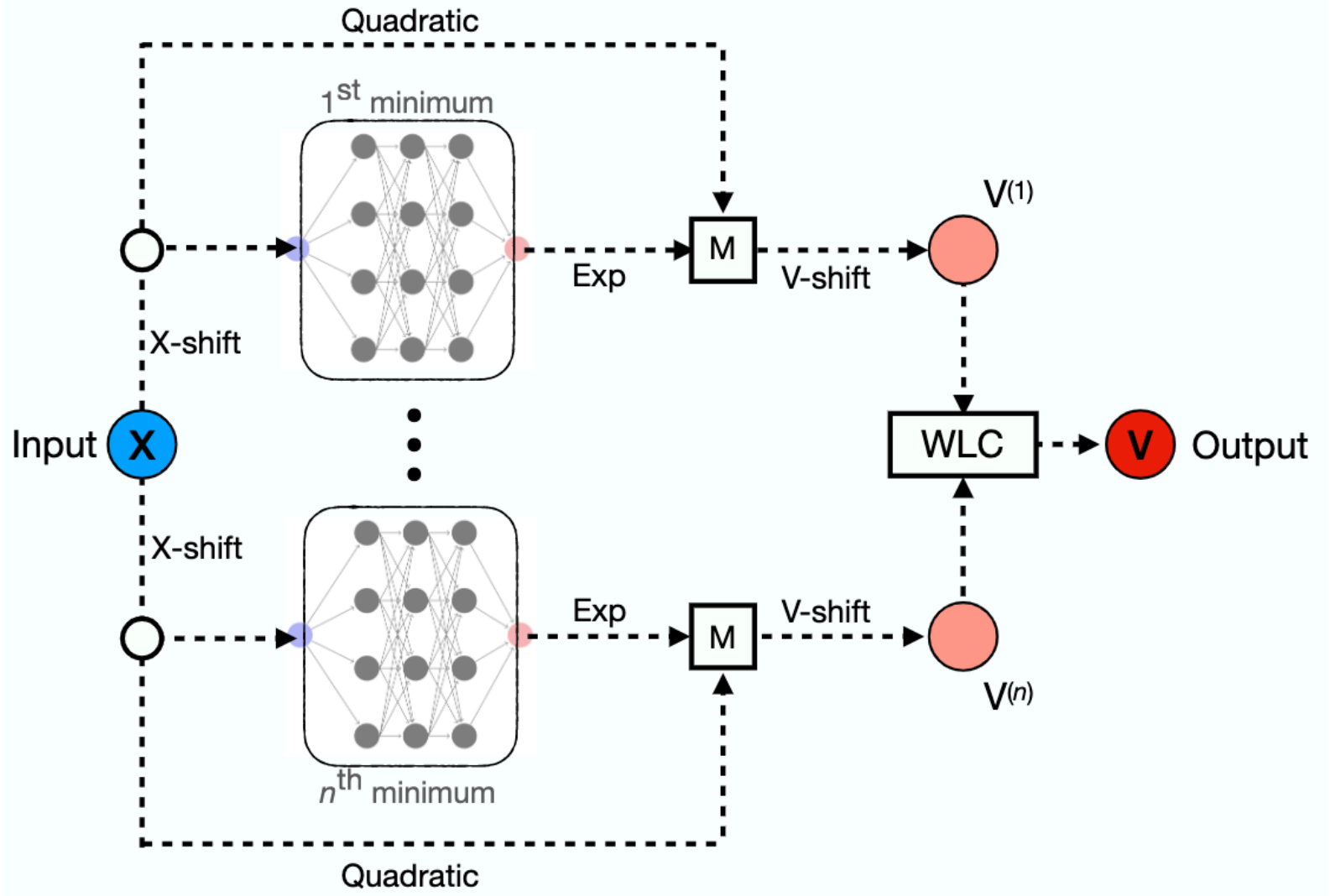
Accurate near the right minimum

$$E_s(x) = \frac{w_1(x)E_1(x) + w_2(x)E_2(x)}{w_1(x) + w_2(x)}$$



Accurate near both minima

Handcrafted NN architecture that is accurate near *multiple* minima



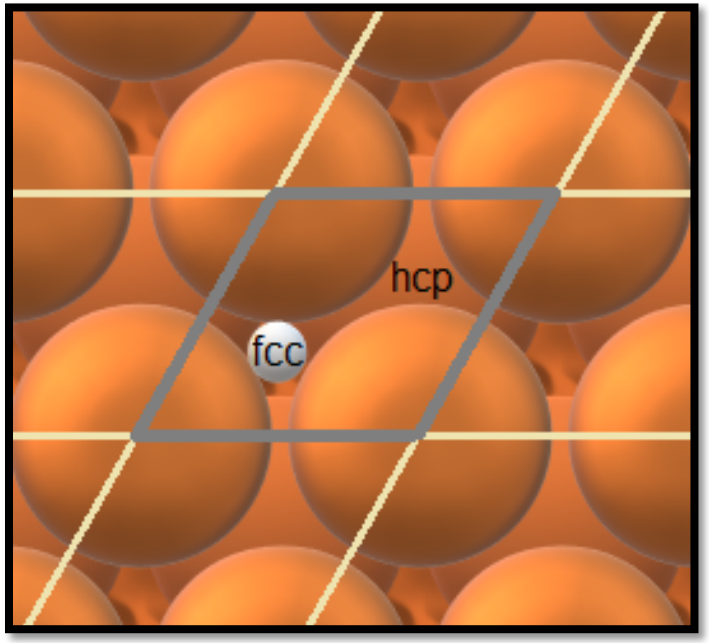
Test case: 3D translation of a H atom on Cu(111)

We utilized the periodicity of the Cu(111) surface by only looking at the area translations of H in a single primitive Cu(111) unit cell.

We generated DFT training data points for a total of

- 14,935 geometries in the case of PBE-D3(ABC)
  Training focused around fcc binding site
- 9,382 geometries in the case of BEEF-vdW
  Training focused around both the fcc and the hcp binding site

Both sets include quasi-random Sobol and multivariate Gaussian distributed points.



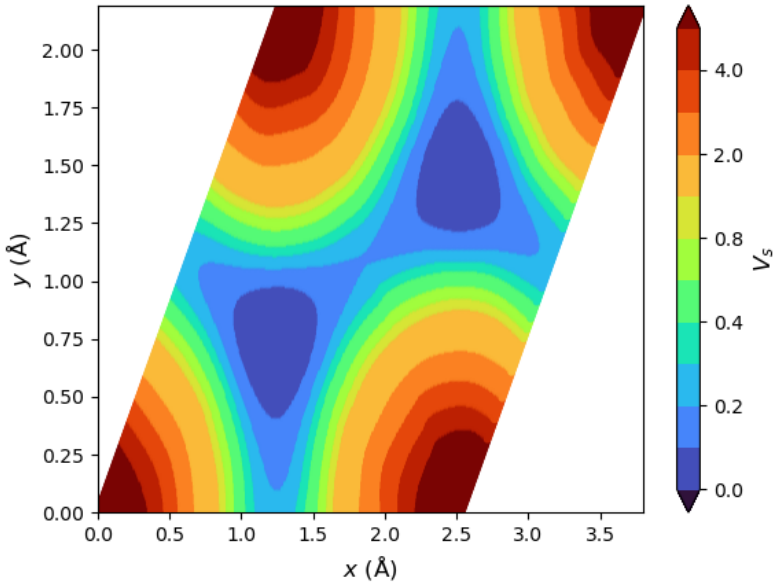
Quantum ESPRESSO

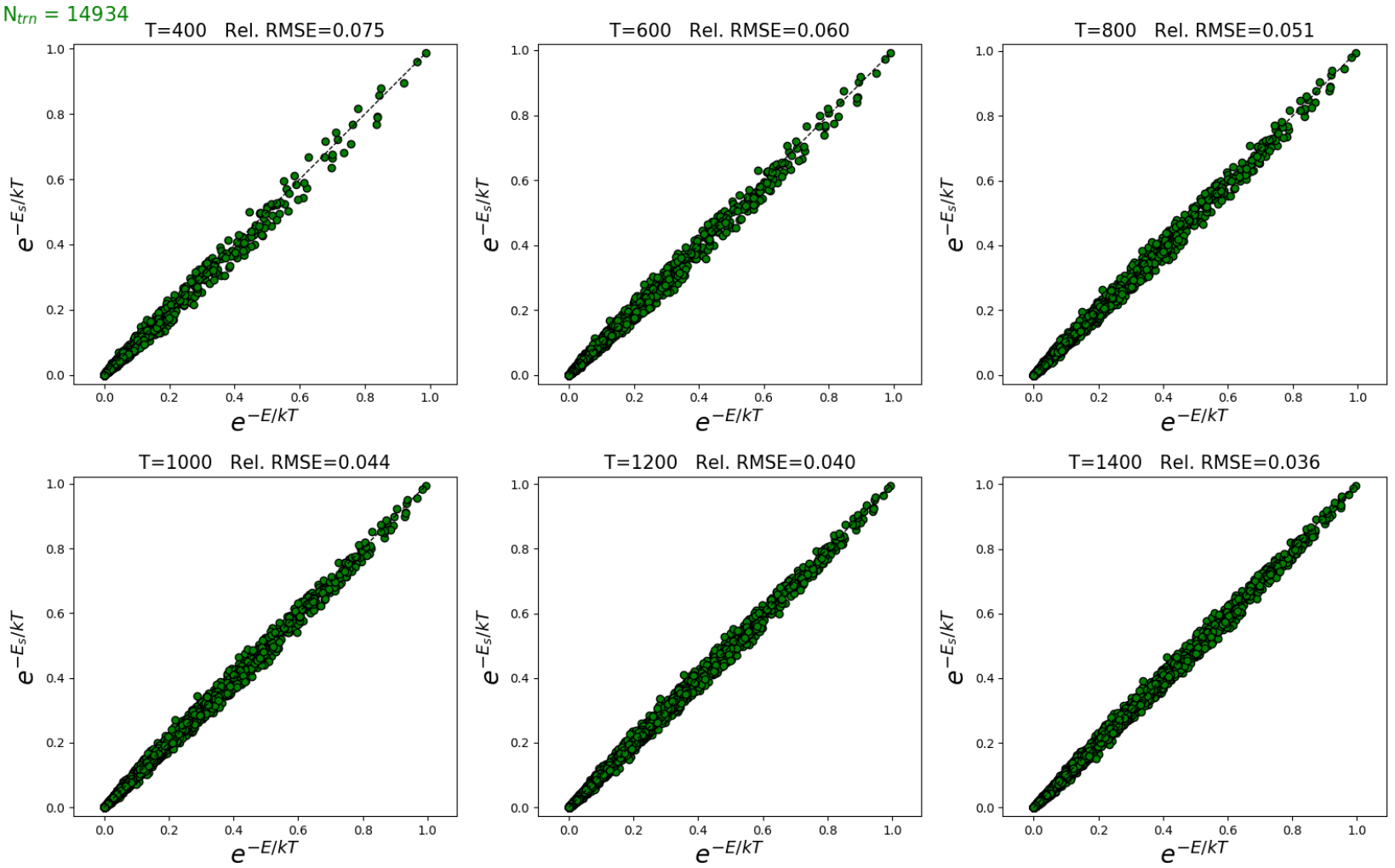
Fixed surface atoms

DFT functionals: PBE-D3(ABC)
BEEF-vdW

MP-NN surrogate construction results for H on Cu111

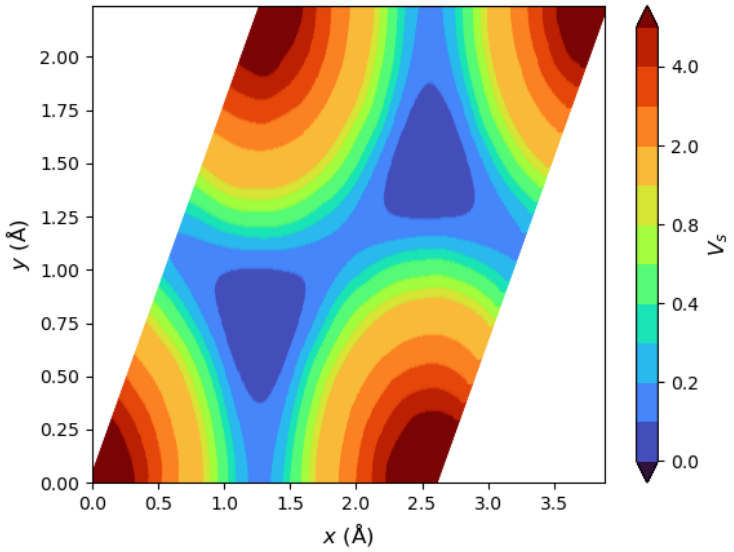
PBE-D3(ABC) result:

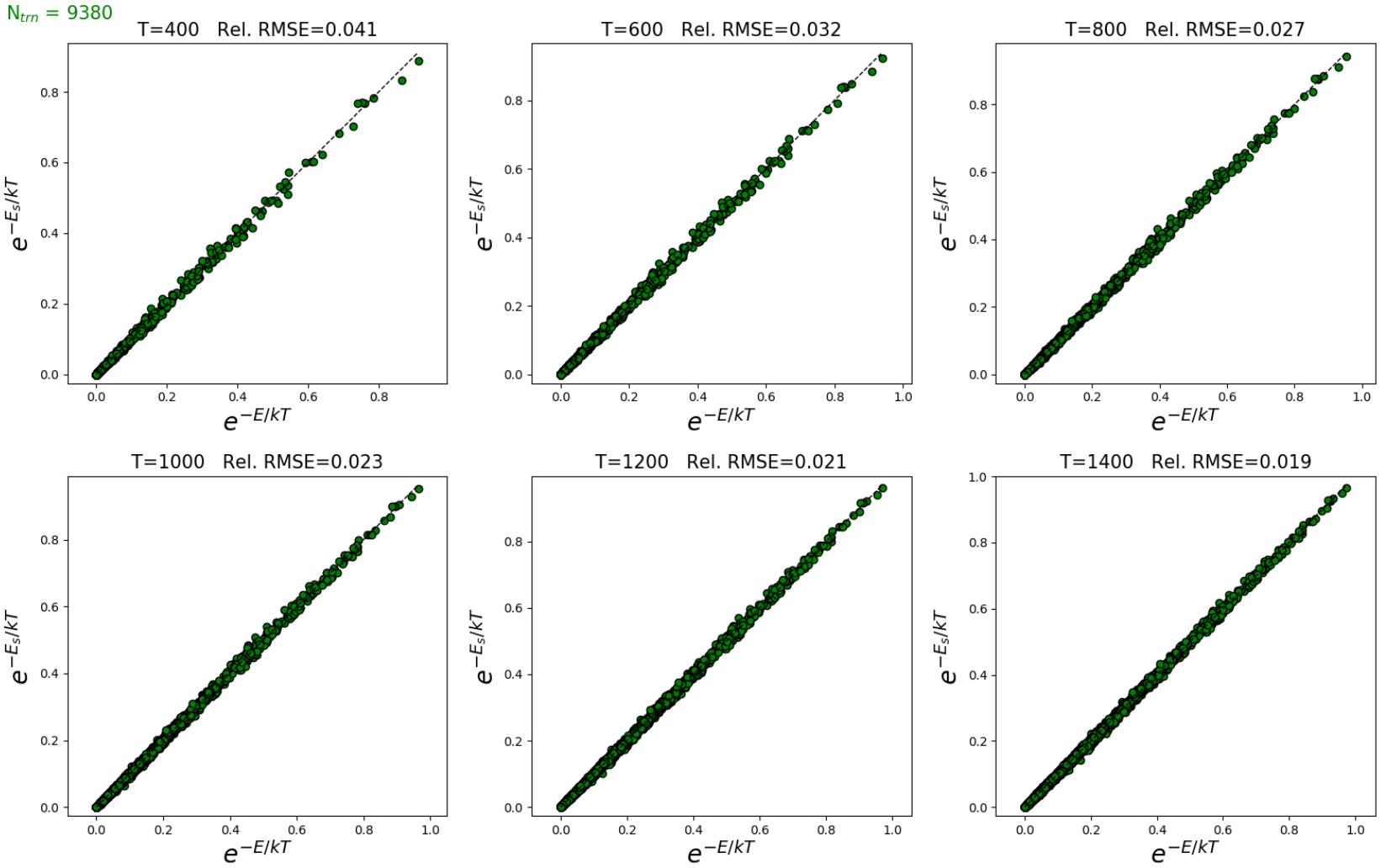




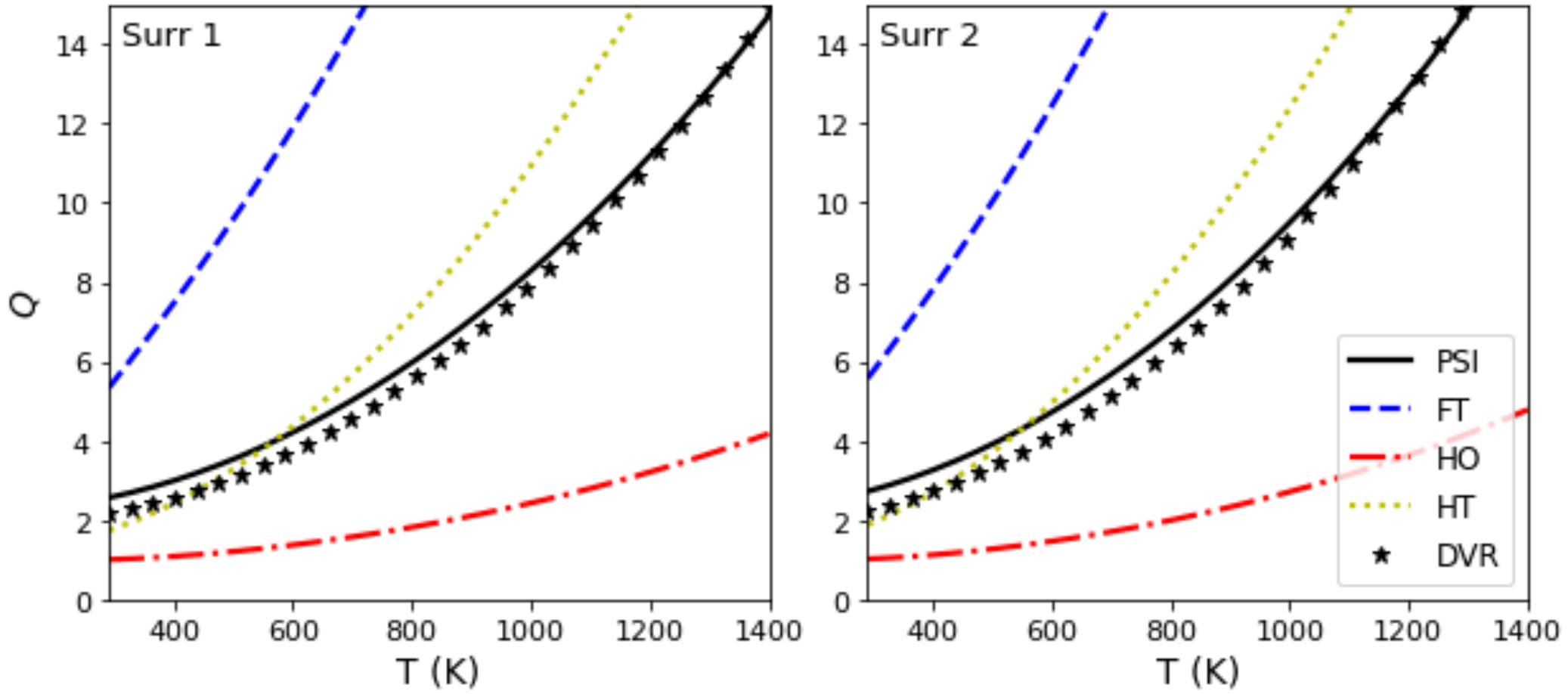
MP-NN surrogate construction results for H on Cu111

BEEF-vdW result:





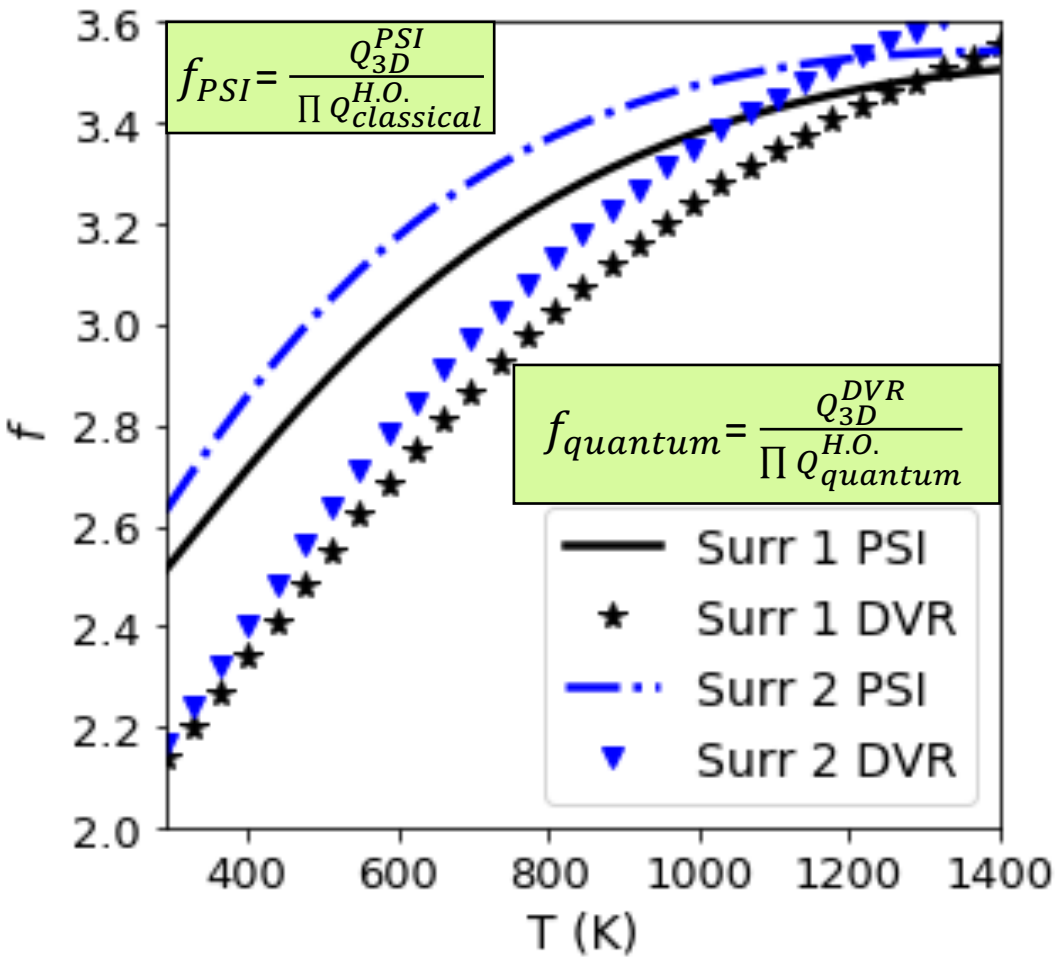
The partition function becomes increasingly anharmonic at higher temperatures



Slide from Katrin Blondal

~4.8 million integration points: 2-3h on 1 CPU core

The anharmonic correction factor *f* shows that the PSI results are in good agreement with direct anharmonic state counting results



Quantum mechanical method:
Discrete variable representation (DVR) calculations carried out on the 2D-PES of a single invariant xy grid and on the 1D z coordinate. The 3D partition function is the product of the direct summations of the eigenstates of the xy degrees of freedom and the z degree of freedom.[1]

The normalization is based on the wavenumbers of H in the MP-NN surrogate fcc position.

ν_x = 880.9 cm^{-1}
ν_y = 881.1 cm^{-1}
ν_z = 1084.8 cm^{-1}

[1]Work of Dr. David H. Bross at Argonne National Laboratory

We obtained the thermodynamic properties by deriving them directly from the partition function

We use analytical expressions[1] to obtain the derivatives of the partition function:

$$Q_{T(C)} = \frac{(2\pi\, m\, k_B T)^{n/2}}{h^n} I_0$$

$$I_0 = \int_{q_1}\int_{q_2}\dots\int_{q_n} e^{-\beta V(q_1,q_2,\dots,q_n)}\, dq_1 dq_2 \dots dq_n$$

$$\frac{[H_T - H_0]_{(C)}}{RT} = \frac{n}{2} + \frac{I_1}{I_0}$$

$$I_1 = \int_{q_1}\int_{q_2}\dots\int_{q_n} \beta\, V(q_1, q_2, \dots, q_n)\, e^{-\beta V(q_1,q_2,\dots,q_n)}\, dq_1 dq_2 \dots dq_n$$

$$\frac{S_{T(C)}}{R} = \frac{n}{2} + \frac{I_1}{I_0} + \ln\left[\frac{(2\pi\, m\, k_B T)^{n/2}}{h^n} I_0\right]$$

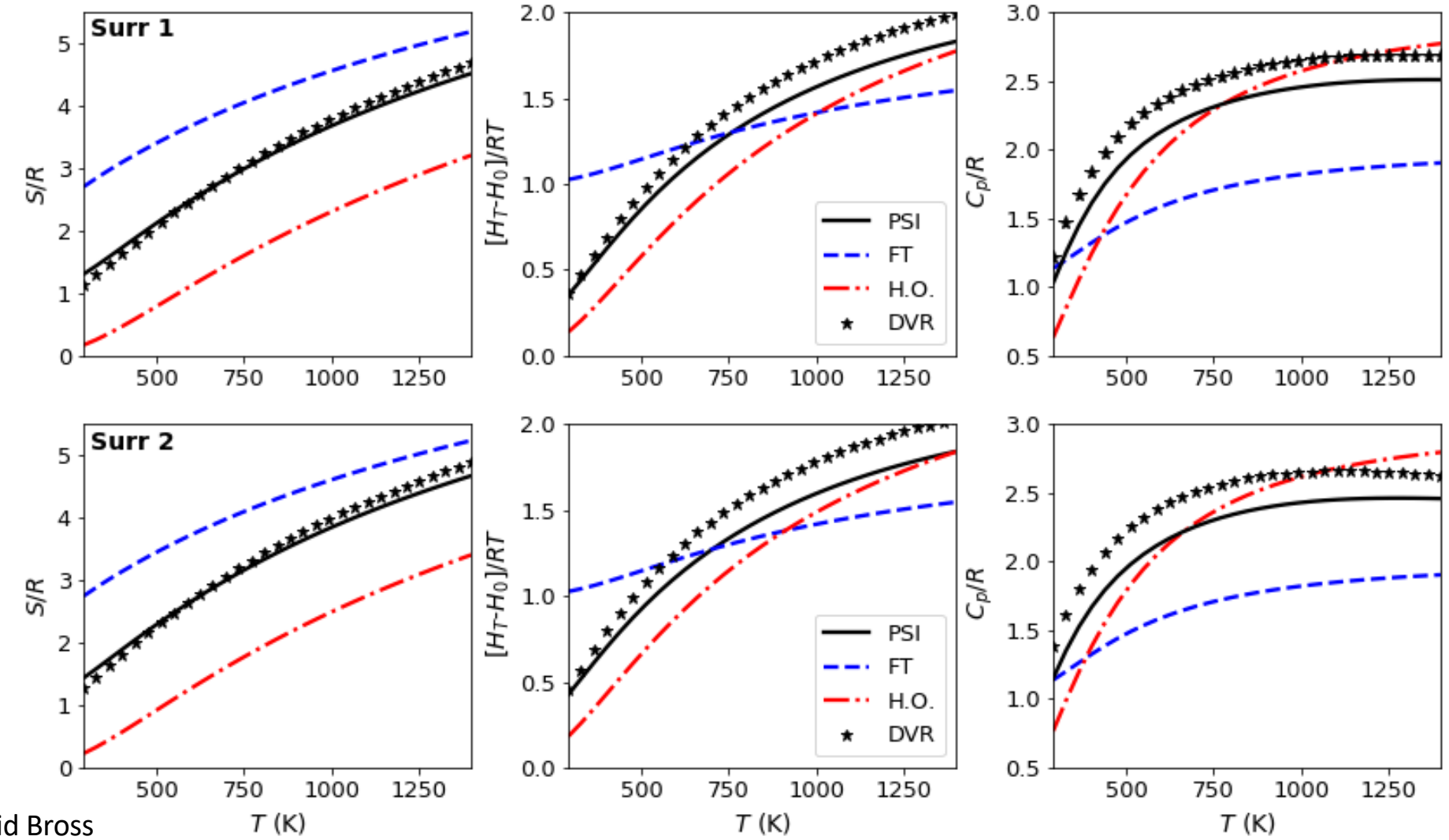
$$\frac{C_{p,T(C)}}{R} = \frac{n}{2} + \frac{I_2}{I_0} - \left(\frac{I_1}{I_0}\right)^2$$

$$I_2 = \int_{q_1}\int_{q_2}\dots\int_{q_n} [\beta\, V(q_1, q_2, \dots, q_n)]^2\, e^{-\beta V(q_1,q_2,\dots,q_n)}\, dq_1 dq_2 \dots dq_n$$

Integrals I_0, I_1, and I_2 are all included in the integration routine

[1]B. Ruscic, D. H. Bross (2019). *Computer-Aided Chemical Engineering, 45*, 3-114

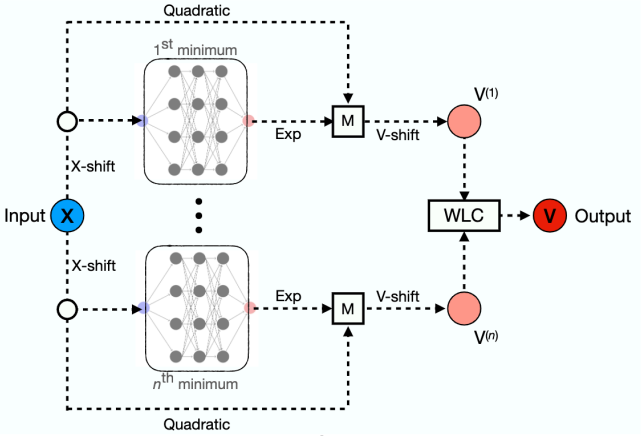
The thermophysical quantities obtained with PSI are substantially different from those predicted by the standard models



Slide from Katrin Blondal and David Bross

Summary: ML

- Hessian-informed DFT sampling
- Minima-preserving neural network (MP-NN) architecture
- Smoothing factor in linear combination of surrogates provides a knob for a trade-off between local accuracy and global smoothness

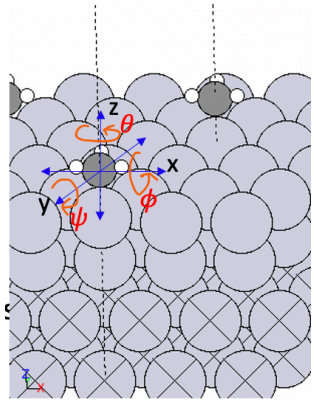


Next:

- Apply to more than two minima
- Formulate a ‘single-shot’ NN training
- Generalize the approach to incorporate saddle points
- Incorporate forces in the training of the handcrafted surrogate form

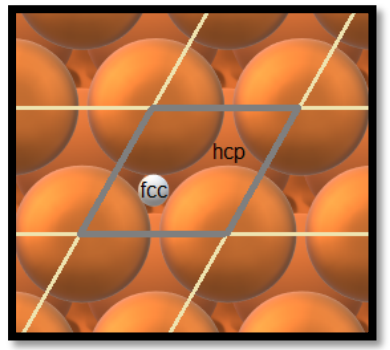
Summary: Chem

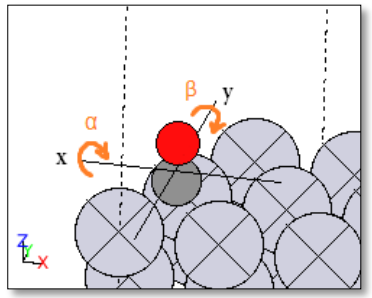
- Applied MP-NN for the partition function calculation for the H on CU(111) case
- Provides approximation with a fraction of the cost
- Excellent agreement with DVR over entire temperature range
- Paper submitted to JPC



Next:

- Develop into standalone robust methodology
  - To obtain anharmonic partition functions for adsorbate-surface systems
  - Open-source code: AdTherm
- Incorporate rotational degrees of freedom
  - Complete 5D case: CO on Pt(111)
  - Complete 6D case: CH_3OH on Cu(111)
- Extend into transition states for surface reactions
- Get coverage dependent partition functions





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