Uncertainty quantification in atomistic simulations

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Outline

- UQ Definitions
- Ab initio and classical interatomic potentials
- Crystal structure prediction
- Conclusions

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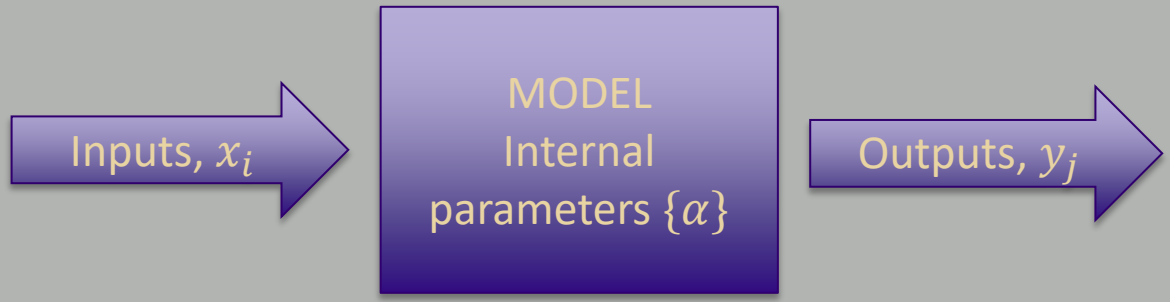
Basic definitions of UQ



Uncertainty Quantification: Δy_j

Verification $y_j \leftrightarrow y_{known}$

Validation $y_j \leftrightarrow y_{experiment}$

Error propagation: $\Delta x_i \rightarrow \Delta y_j$

Sensitivity analysis

Model calibration

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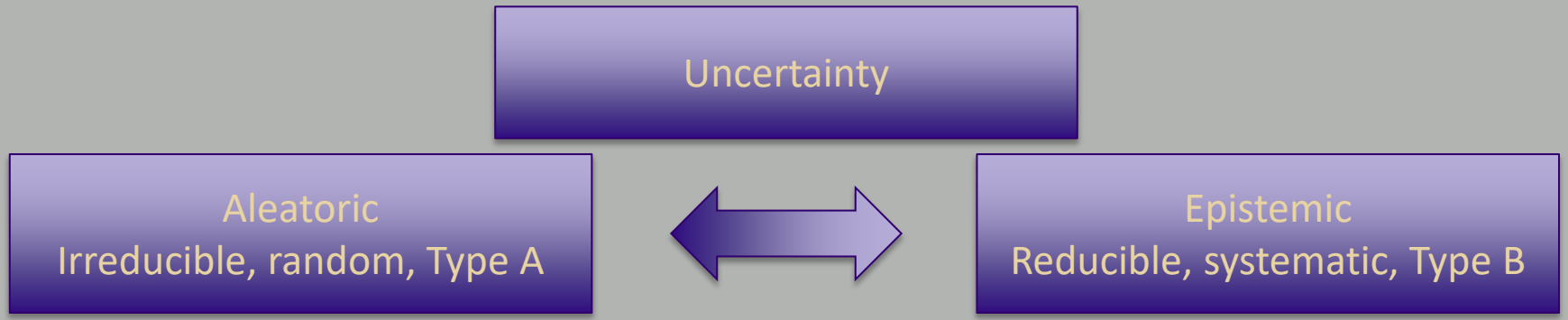
Errors classification



- Random measurement error
- Thermal fluctuations
- Stochastic algorithms

- Incomplete theory or inadequate model
- Bias in numerical algorithms
- Round-off errors

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UQ

Donald Ramsfield, then secretary of defense:

“Reports that say that something hasn't happened are always interesting to me, because as we know, there are **known knowns**; there are things we know we know. We also know there are **known unknowns**; that is to say we know there are some things we do not know. But there are also **unknown unknowns**—the ones we don't know we don't know. And if one looks throughout the history of our country and other free countries, it is the latter category that tends to be the difficult ones.”

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Simple example: pendulum as a clock

Huygens: ~1650: $\boldsymbol{T^2 \sim l}$, First pendulum clock (~100° *amplitude*)

~ 60 sec per day

Hooke, Newton: ~1700: Small amplitude: $\boldsymbol{T = 2\pi\sqrt{\frac{l}{g}}}$

Uncertanties: Model: **Epistemic;** Length measurement: **aleatoric;** g: constant, poorly defined/measured: **epistemic**

~10 sec per day

Graham: 1721: Correction for thermal expansion: makes uncertainty in length epistemic!

Bernoulli: 1741: Correction to the model: $T = 2\pi\sqrt{\frac{l}{g}}\left(1 + \frac{1}{16}\theta_0^2 + ..\right)$

Buoyancy force, advancement in the escapement mechanism, drag effect, local gravity etc…:

~1 sec per year; Most precise clocks till quartz

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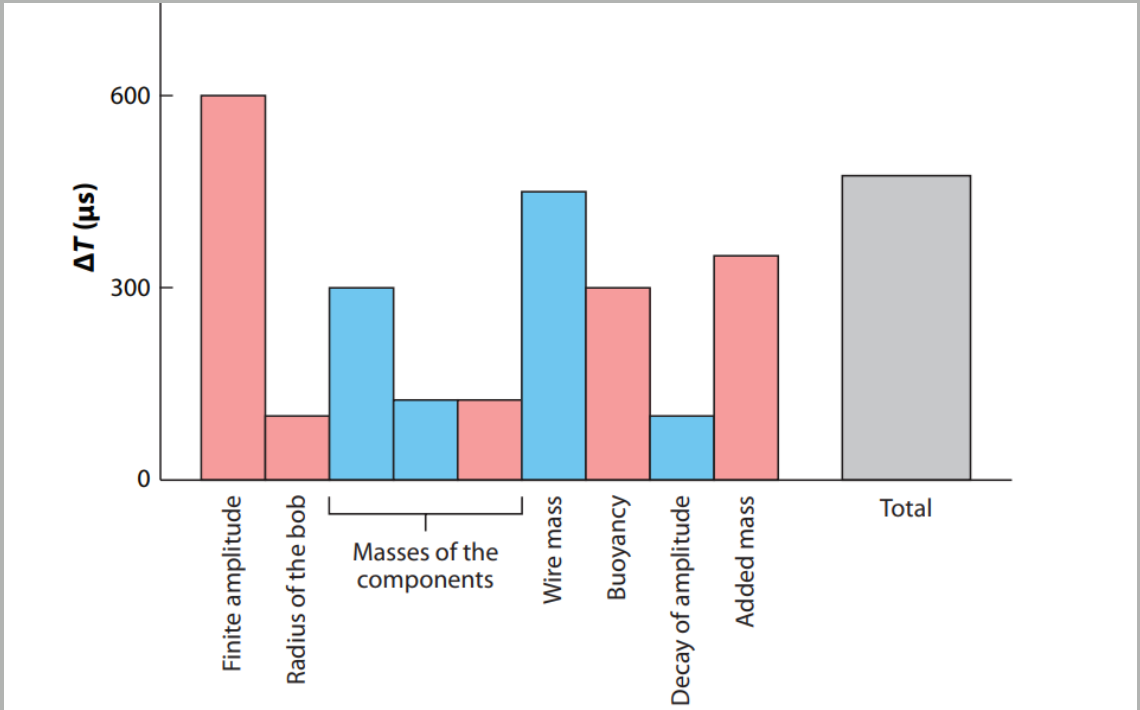
Modern analysis



Nelson RA, Olsson MG. 1986. The pendulum: rich physics from a simple system. Am. J. Phys. 54:112–21

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Metrology: the values of fundamental constants

- SI system steadily redefines fundamental units so that their measurements can be more accurate and independent of artefacts:
  - Second: Fraction of a day -> Fractions of the year -> frequency associated with the Cs^{133} atomic transitions
  - Meter: Fraction of the Earth circumference -> Artifacts -> Using unit of time and the speed of light: Makes speed of light precise.
  - Kilogram: Mass of 1 litre of water -> Artefacts -> Using time and length and fixing Plank's constant.

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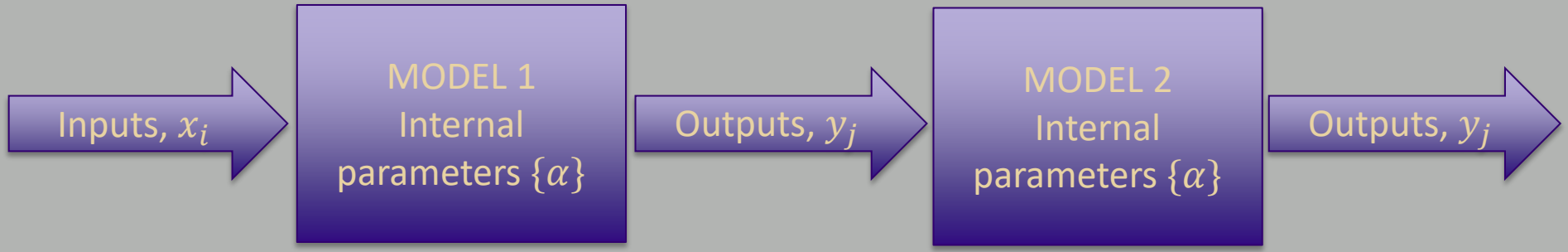
Multiscale simulations in materials science



- 15 orders of magnitude in time and 10 orders of magnitude in length between atomic and macroscopic scales: More that 2 models are common.
- Propagation of errors is very important.

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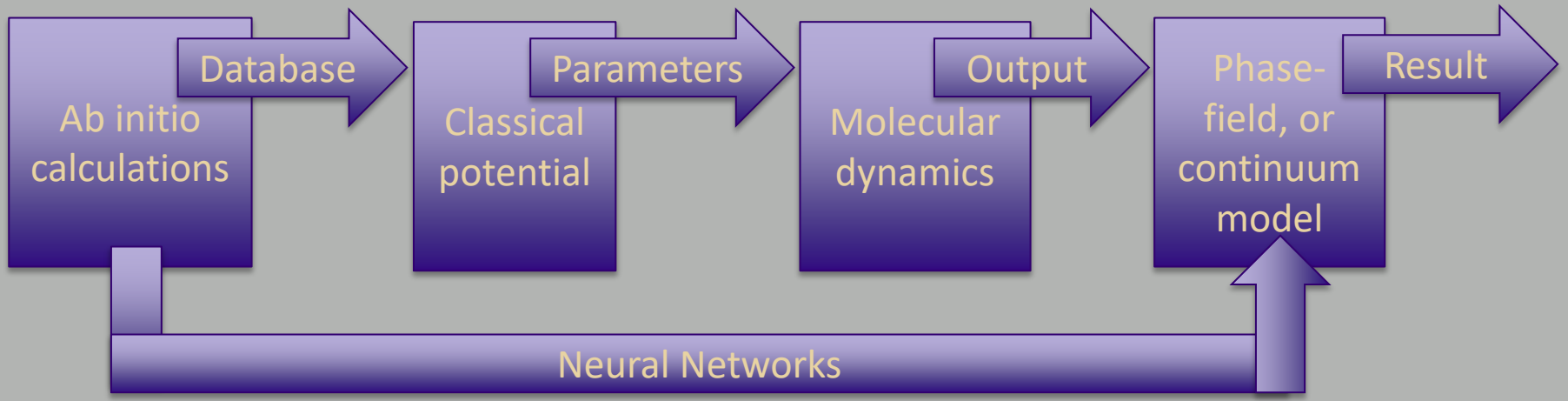
Typical example



- One can stop at any point
- Multiscale can be concurrent, i.e. atomic level simulations are performed on the fly when needed, or sequential.
- Large number of community codes these days make these simulation very common

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DFT verification

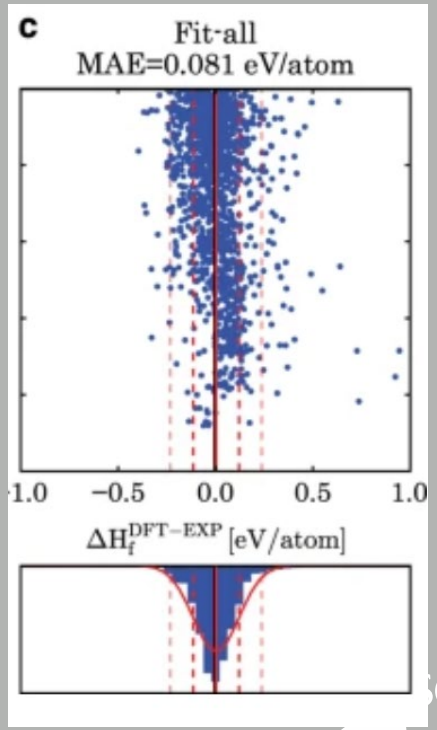
- How correctly do we solve the equations?
- There are multiple implementations, one can compare
- Popular modern implementations differ from each-other less than experimental uncertainties

		average <Δ>	AE: Elk	AE: exciting	AE: FHI-aims/tier2	AE: FLEUR	AE: FPLO/T+F+s	AE: RSPt	AE: WIEN2k/acc
AE	Elk	0.6		0.3	0.3	0.6	1.0	0.9	0.3
	exciting	0.5	0.3		0.1	0.5	0.9	0.8	0.2
	FHI-aims/tier2	0.5	0.3	0.1		0.5	0.9	0.8	0.2
	FLEUR	0.6	0.6	0.5	0.5		0.8	0.6	0.4
	FPLO/T+F+s	0.9	1.0	0.9	0.9	0.8		0.9	0.9
	RSPt	0.8	0.9	0.8	0.8	0.6	0.9		0.8
	WIEN2k/acc	0.5	0.3	0.2	0.2	0.4	0.9	0.8	
PAW	GBRV12/ABINIT	0.9	0.9	0.8	0.8	0.9	1.3	1.1	0.8
	GPAW09/ABINIT	1.4	1.3	1.3	1.3	1.3	1.7	1.5	1.3
	GPAW09/GPAW	1.6	1.5	1.5	1.5	1.5	1.8	1.7	1.5
	JTH02/ABINIT	0.6	0.6	0.6	0.6	0.6	0.9	0.7	0.5
	PSlib100/QE	0.9	0.9	0.8	0.8	0.8	1.3	1.1	0.8
	VASPGW2015/VASP	0.6	0.4	0.4	0.4	0.6	1.0	0.8	0.3

K. Lejaeghere et al., Science 351, aad3000 (2016).

DFT validation: just how good is it?

- Comparison of DFT with experiment over large dataset
- 1670 compounds evaluated
- All reference states are evaluated and “adjusted”
- Cohesive energy MAE: 0.081 eV/A



Kirklin et al, npj Computational Materials **1**, 15010 (2015)

UQ in Density Functional Theory

- UQ of the Generalized Gradient Approximation to the Density functional theory.

$$Atomic\ Positions\ \vec{R}_i \rightarrow v(\vec{r}) \xrightarrow{DFT} E[n_e, \vec{\nabla} n_e]$$

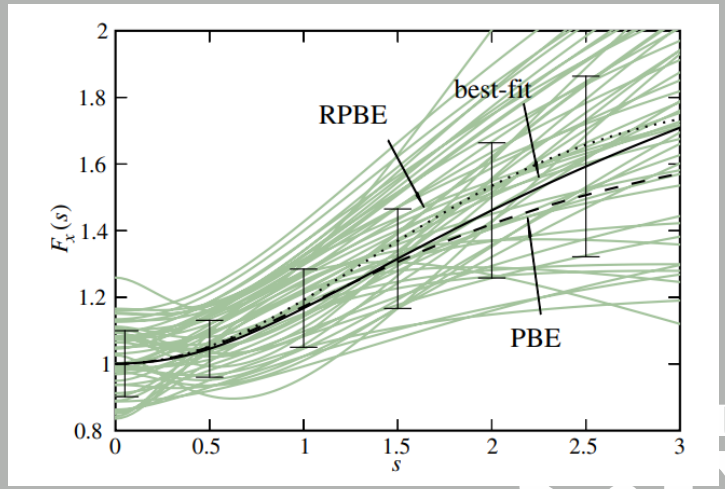
- Experimental observables: $\Delta E, \vec{R}@\min E$
- ∇n_e enters as a function $F_x = F_x(\theta_i), i = 1..3$

- θ_i are sampled from:

$$\rho \sim \exp(-C(\theta_i)/T)$$

$$C(\theta) = \sum (O_{obs} - O_{calc})^2$$

Minimize $C(\theta)$, and set $T = C_{min}$.

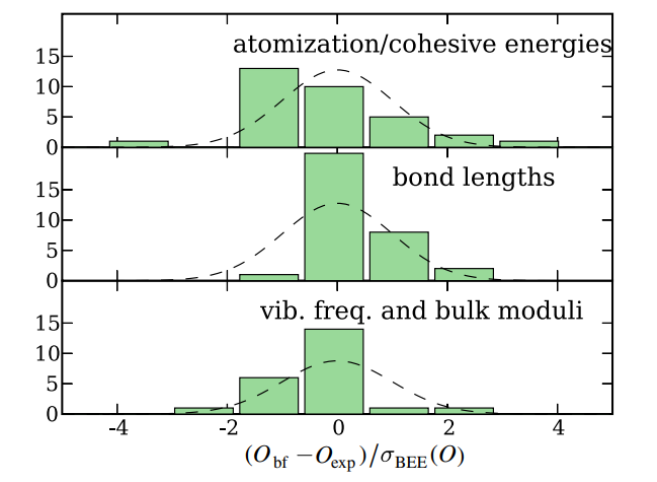


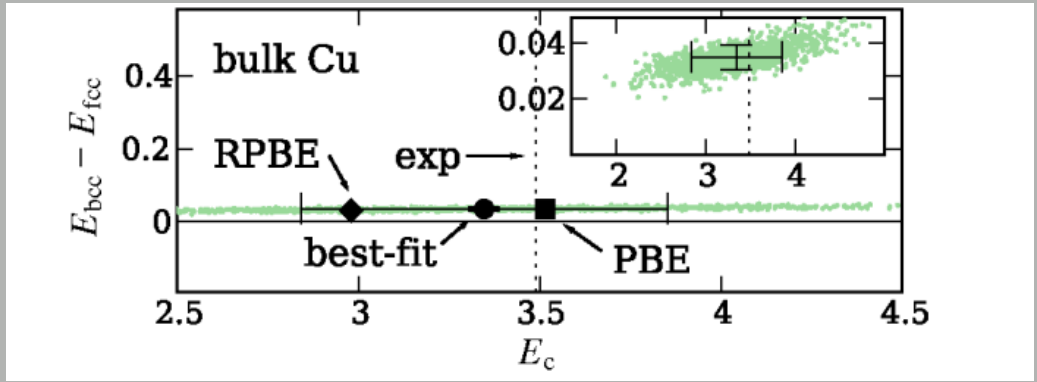
Mortensen et al, PRL 95, 216401 (2005)

Ensemble UQ in Density Functional Theory

> UQ of the Generalized Gradient Approximation to the Density functional theory.

$$Atomic\ Positions\ \vec{R}_i \rightarrow v(\vec{r}) \xrightarrow{DFT} E[n_e, \vec{\nabla} n_e]$$





Mortensen et al, PRL 95, 216401 (2005)

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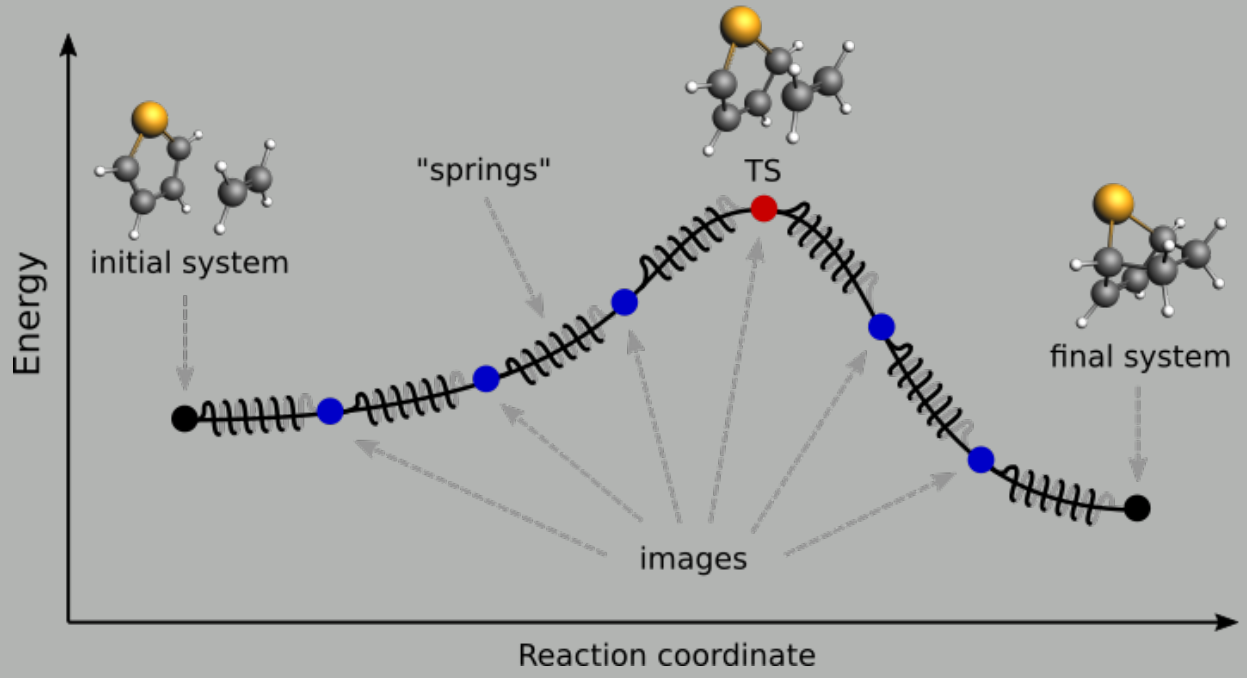
UQ & GP in Nudge Elastic Band with DFT



https://www.scm.com/doc/AMS/Tasks/NEB.html

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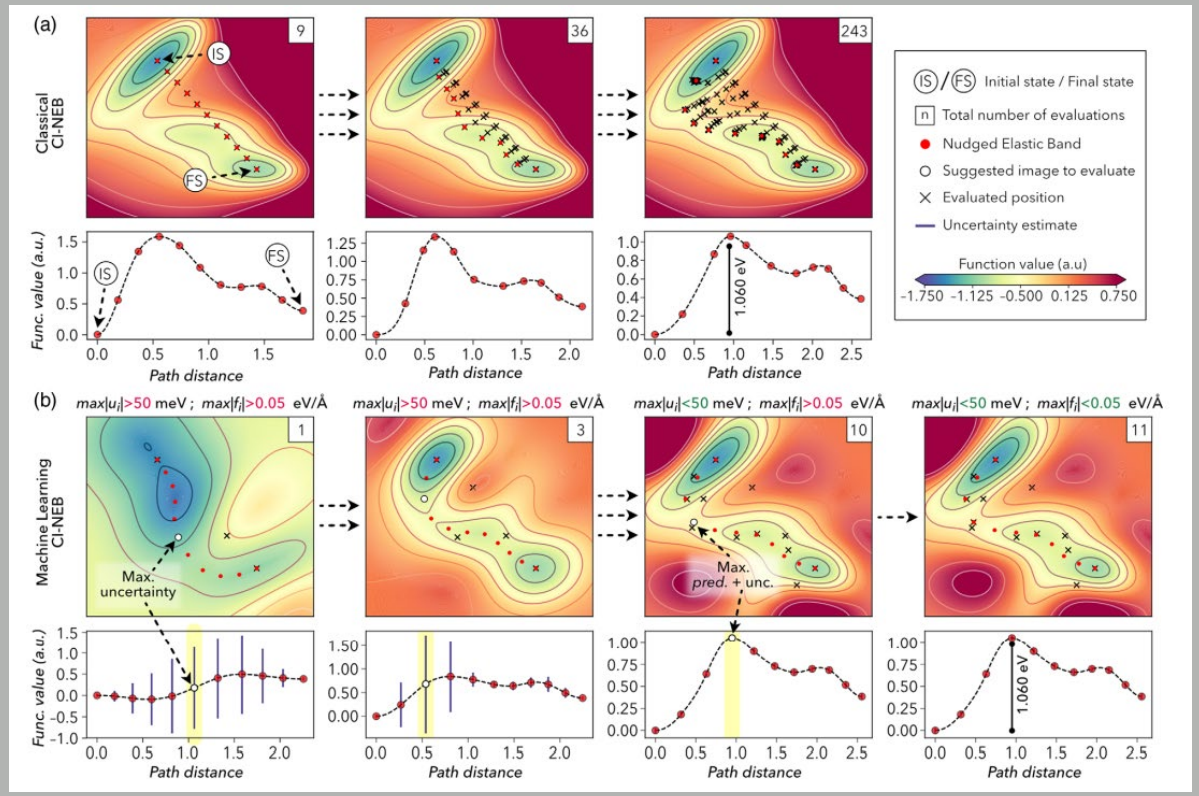
UQ & GP in Nudge Elastic Band with DFT



- Fit GP model by using DFT on first iterations.
- Use GP model to estimate uncertainty at each image
- Move the images, do DFT at the most uncertain image
- Refit the model and continue
- Order of magnitude reduction in compute

Torres et al, PRL, 122 156001 (2019)

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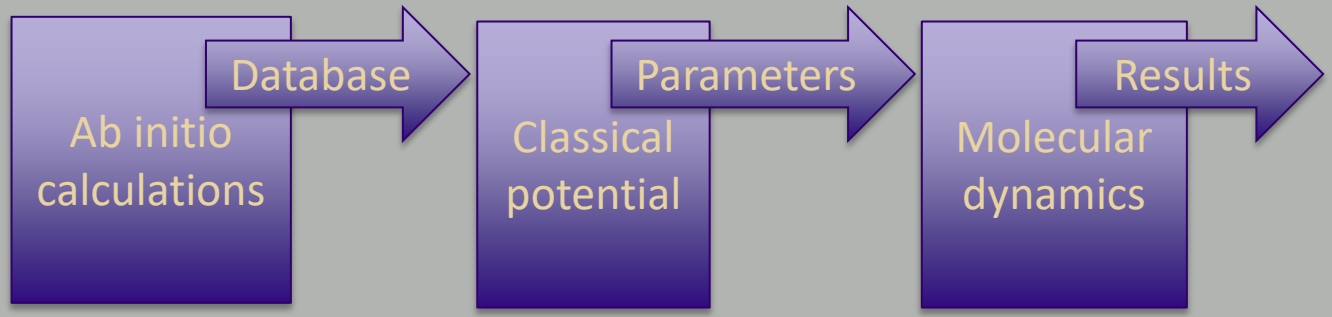
Classical potentials



- Definitely inadequate model
- Parameters are not unique: ~30 parametrization for UO_2 in the literature!

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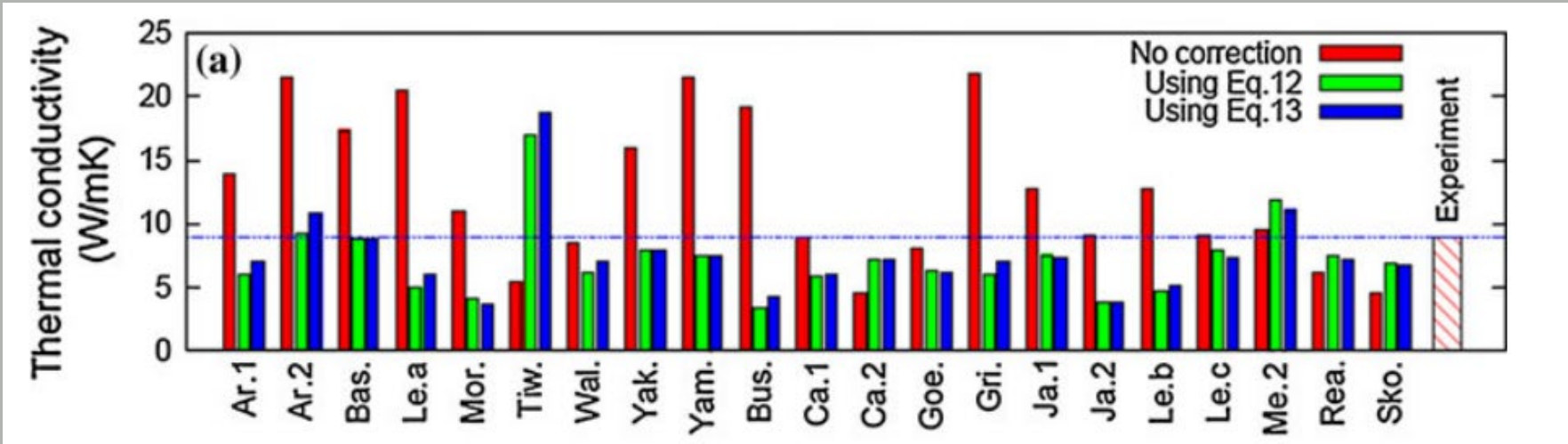
Thermal conductivity as unfitted property



Large variations in almost any unfitted property: use with care!

Chernatynskiy et al, J Mater Sci (2012) 47:7693–7702

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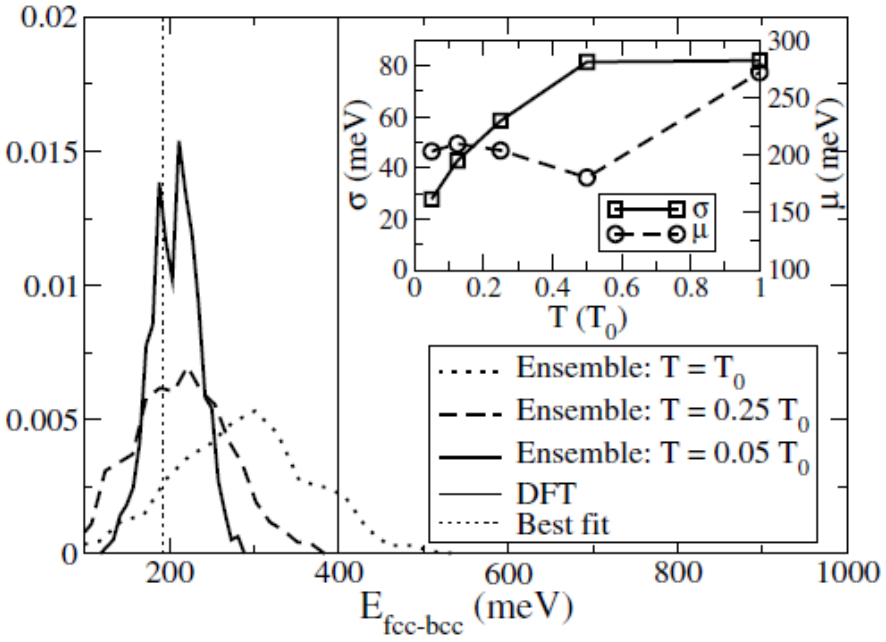
Parameters from distributions: MEAM potentials



- Parameters are sampled from:

$$\rho \sim \exp(-C(\theta_i)/T)$$

$$C(\theta) = \sum(O_{obs} - O_{calc})^2$$

Minimize $C(\theta)$, and set $T_0 = C_{min}$.

Frederiksen et al, PRL 93, 165501 (2004)

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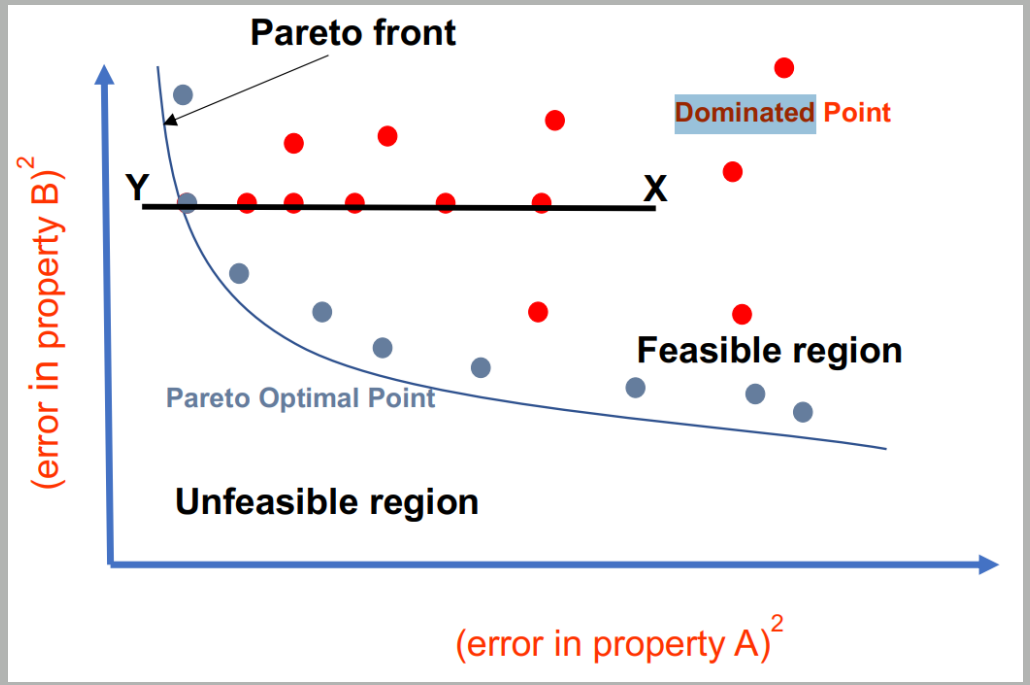
Pareto-optimization for potentials



Sample potential space

Identify approximate Pareto front

Preferentially sample near Pareto front

Generate sample of Pareto-optimal potentials

$F = \left((\Delta A)^2 + (\Delta B)^2\right)$: No (arbitrary) weights!

Ragasa et al 2019 Modelling Simul. Mater. Sci. Eng. 27 074007

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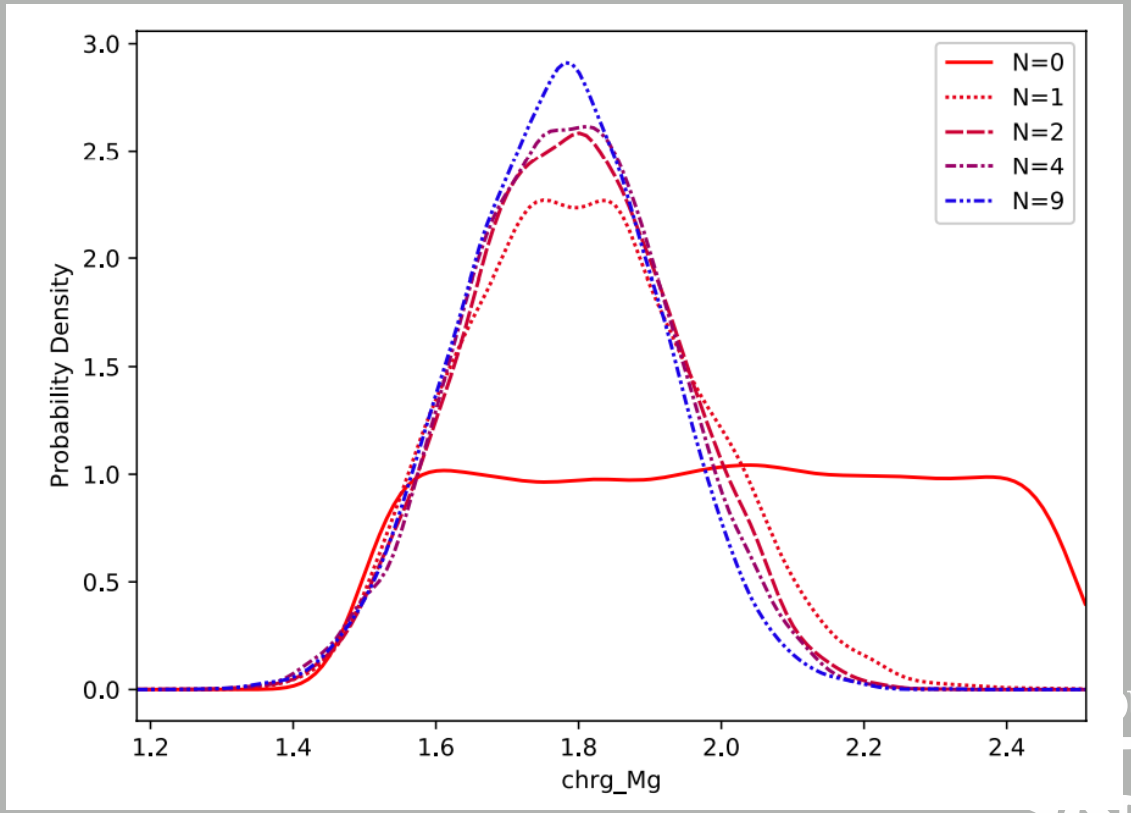
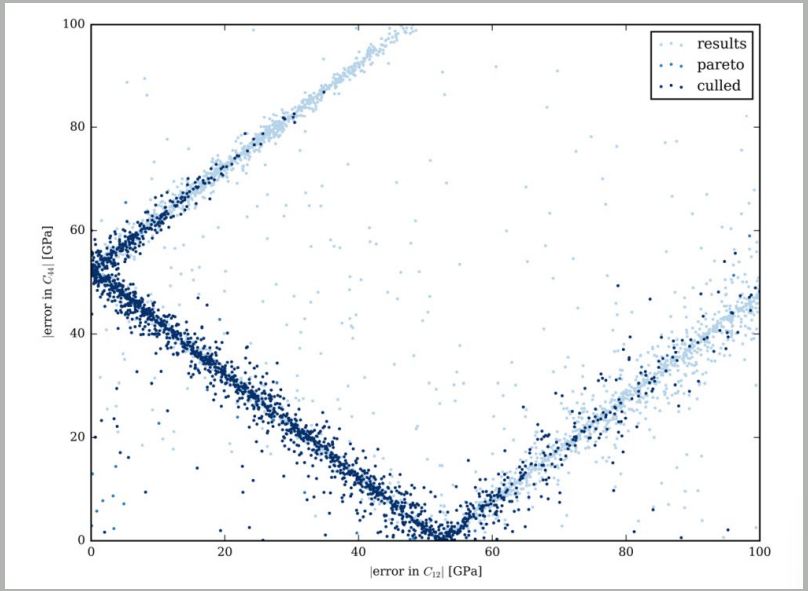
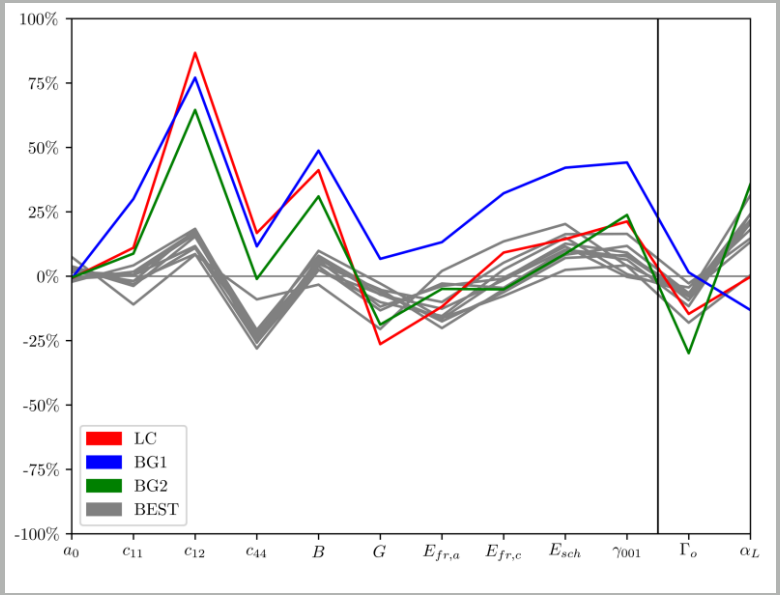
Probability distribution evolution

- Uninformed prior develops preference for a specific value due to improved approximations to the Pareto front.



Pareto-optimal sample





Ragasa et al 2019 Modelling Simul. Mater. Sci. Eng. 27 074007

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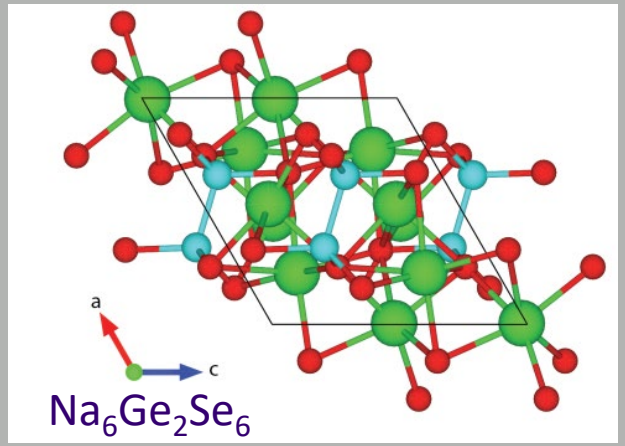
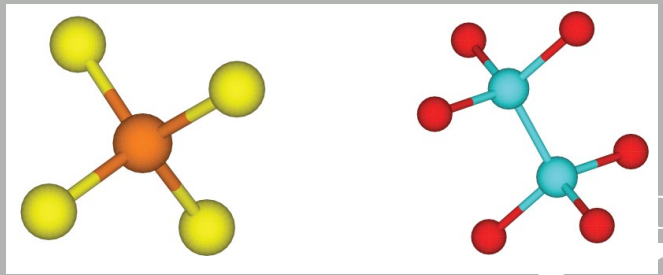
Crystal structure prediction

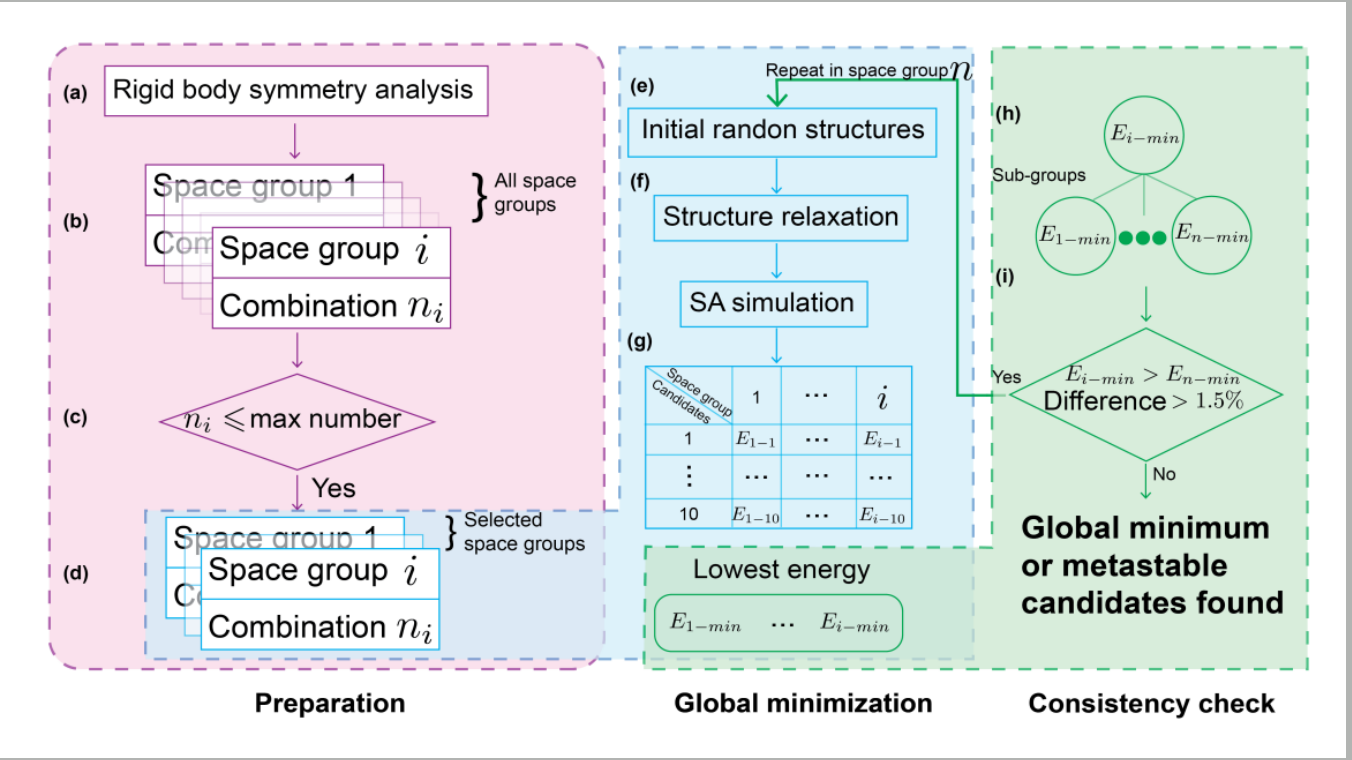
- We are interested in complex chalcogenide compounds for energy applications.
- Use traditional symmetry enabled dimensionality reduction
- Use rigid-block to reduce the dimensionality





Qi Zhang *et al* 2025 *J. Phys.: Condens. Matter* **37** 095901

Overview of the method



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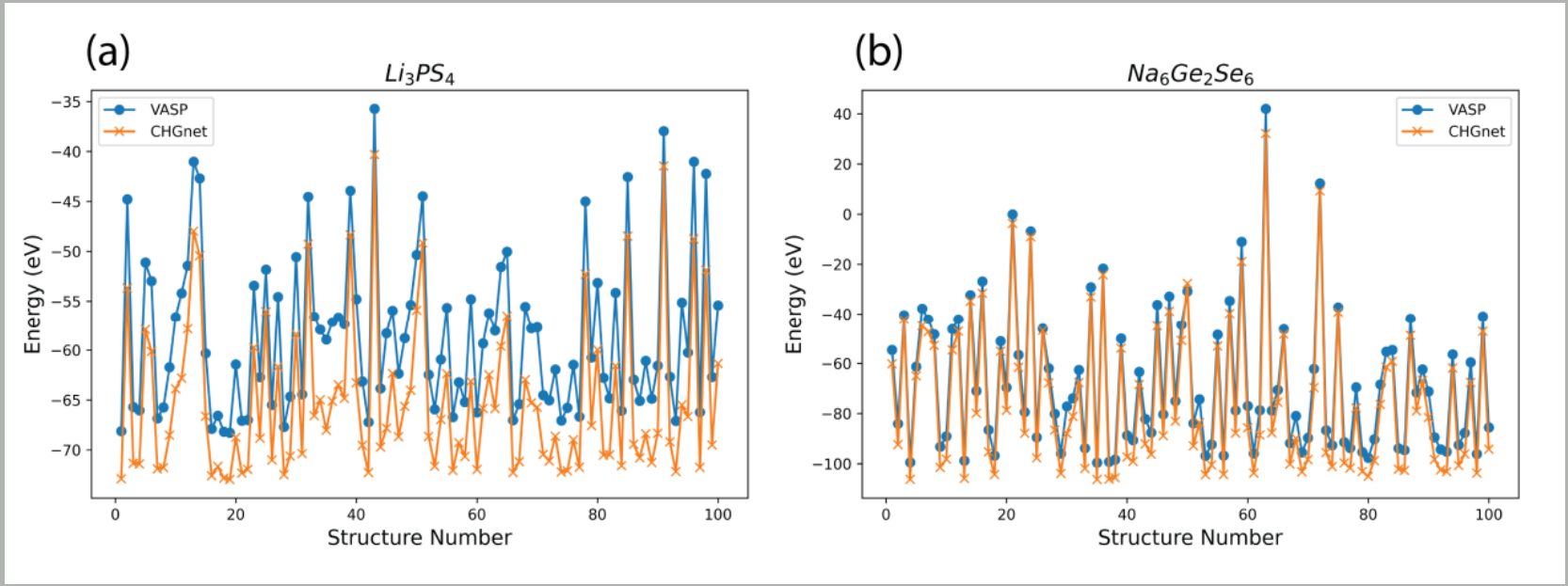
Neural-Network Potentials (CHGNET) as an energy estimator



Good performance from CHGNET potential, possibility for fine-tuning

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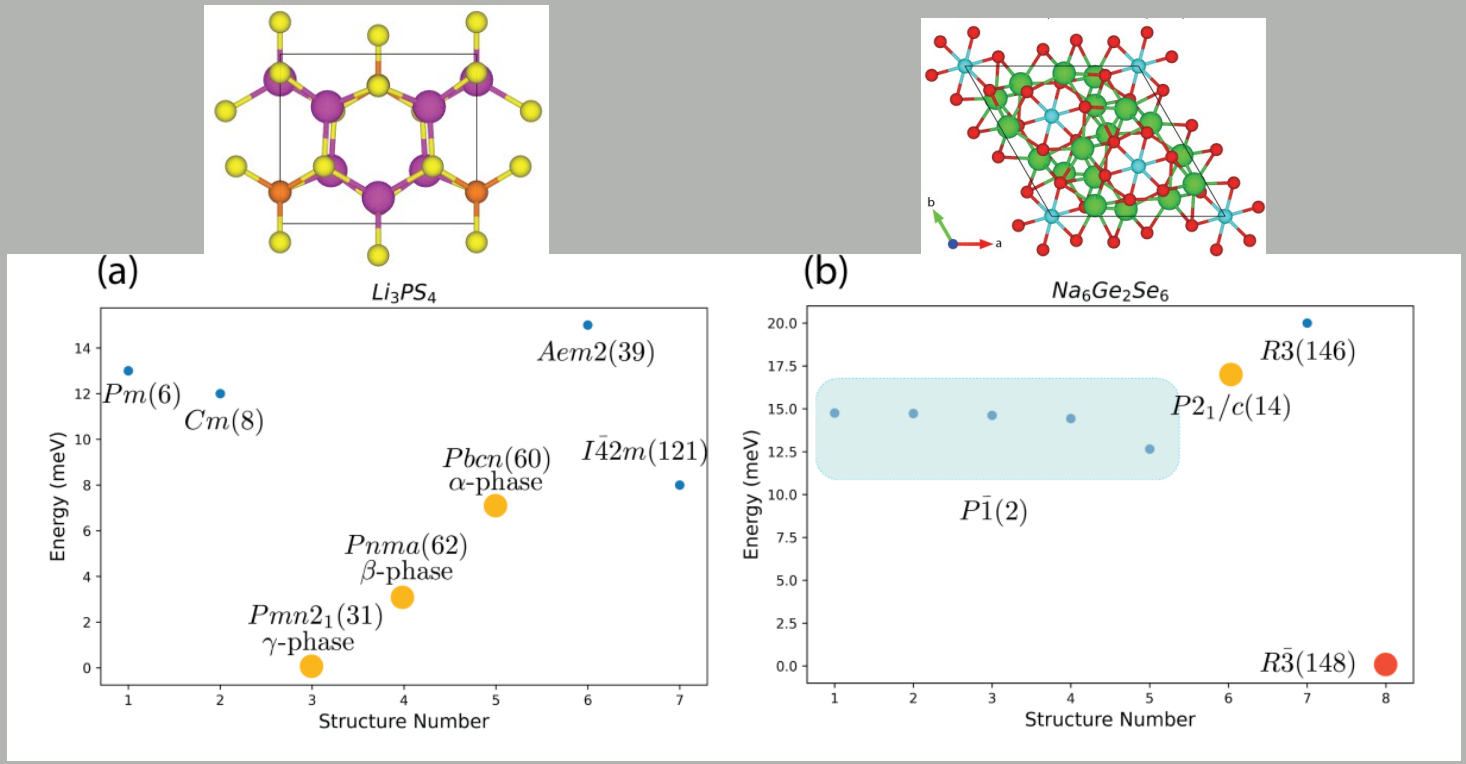
Energies of the predicted structures



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Conclusions

- Broad UQ for atomistic simulations making significant progress.
- DFT theory is well validated and verified, but may be more can be done for UQ
- UQ in classic interatomic potentials are still not fully understood.
- NN potentials are currently in between potentials of old and DFT.

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