Interatomic potentials with error bars

Gábor Csányi
Engineering Laboratory

UNIVERSITY OF
CAMBRIDGE

What makes a potential

Ingredients		Desirable properties
• Representation of atomic neighbourhood	⟶	smoothness, faithfulness, continuity
• Interpolation of functions	⟶	flexible but smooth functional form, few sensible parameters
• Database of configurations	⟶	predictive power non-domain specific

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Fit a function $f(x)$ based on observations $\mathbf{y} \equiv \{y_i\}$ at $\{x_i\}$

$$f(x) = \sum_{i=1}^{N} \alpha_i k(x_i, x) \qquad \text{e.g. } k(x, x') = \sigma_w^2 e^{-|x-x'|^2/2\sigma^2}$$

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regularised fit:
arbitrary σ,σ_w,σ_ν

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$$\mathbf{y} = (\mathbf{K} + \sigma_\nu^2 \mathbf{I})\boldsymbol{\alpha}$$

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Machine learning framework: Kernel regression

$$\varepsilon(\mathbf{q}^{(i)}) = \sum_k^N \alpha_k K(\mathbf{q}^{(i)}, \mathbf{q}^{(k)})$$

- Linear regression:

$$K_{\mathrm{DP}}(\mathbf{q}^{(i)}, \mathbf{q}^{(k)}) = \mathbf{q}^{(i)} \cdot \mathbf{q}^{(k)} \quad \longrightarrow \quad \varepsilon(\mathbf{q}^{(i)}) = \sum_j q_j^{(i)} \sum_k^N \alpha_k q_j^{(k)} = \mathbf{q}^{(i)} \cdot \boldsymbol{\beta}$$

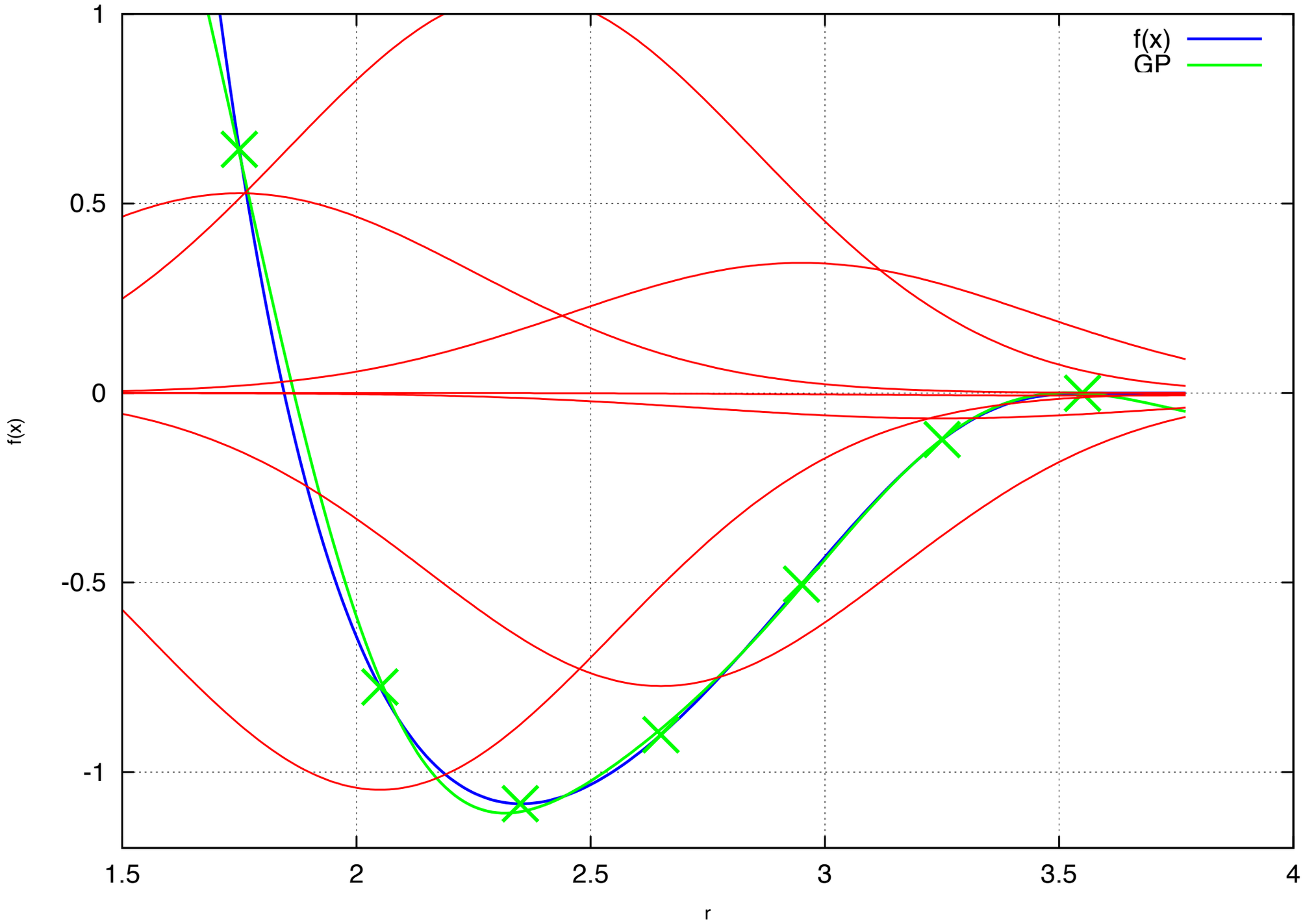
- Neural networks

$$K_{\mathrm{NN}}(\mathbf{q}^{(i)}, \mathbf{q}^{(k)}) = -|\mathbf{q}^{(i)} - \mathbf{q}^{(k)}|^2 + \mathrm{const.}$$

- Gaussian kernel

$$K_{\mathrm{SE}}(\mathbf{q}^{(i)}, \mathbf{q}^{(k)}) = \exp\left(-\sum_j \frac{(q^{(i)} - q^{(k)})^2}{2\sigma_j^2}\right)$$

1D example

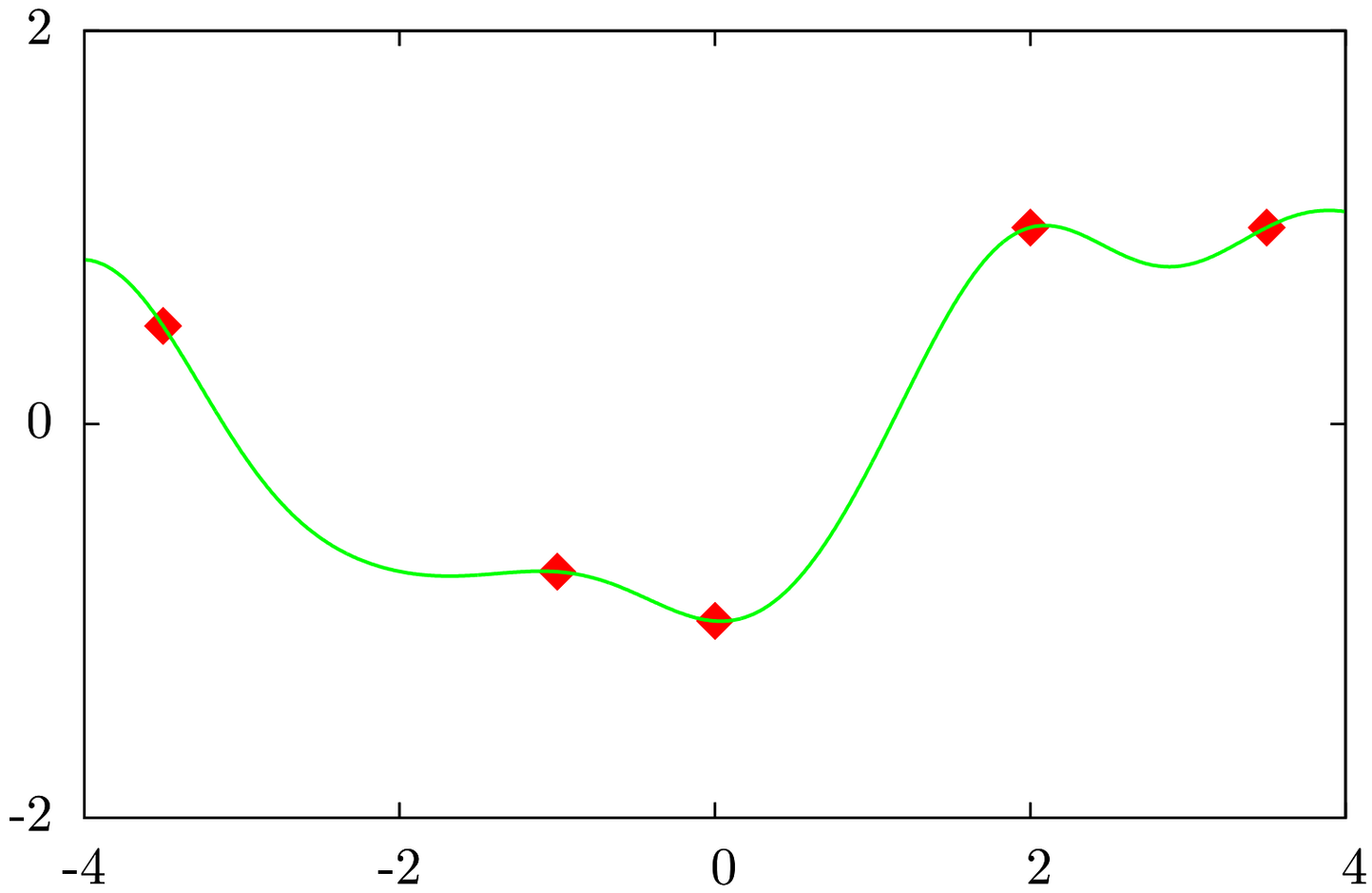


Gaussians basis functions are wide!

$$f(x) = \mathbf{k}^T \mathbf{C}^{-1} \mathbf{y}$$

Samples from Gaussian posterior

$$P(y_{N+1}|\mathbf{y}) \propto \mathrm{Normal}(\mathbf{k}^T\mathbf{C}^{-1}\mathbf{y}, \ldots)$$



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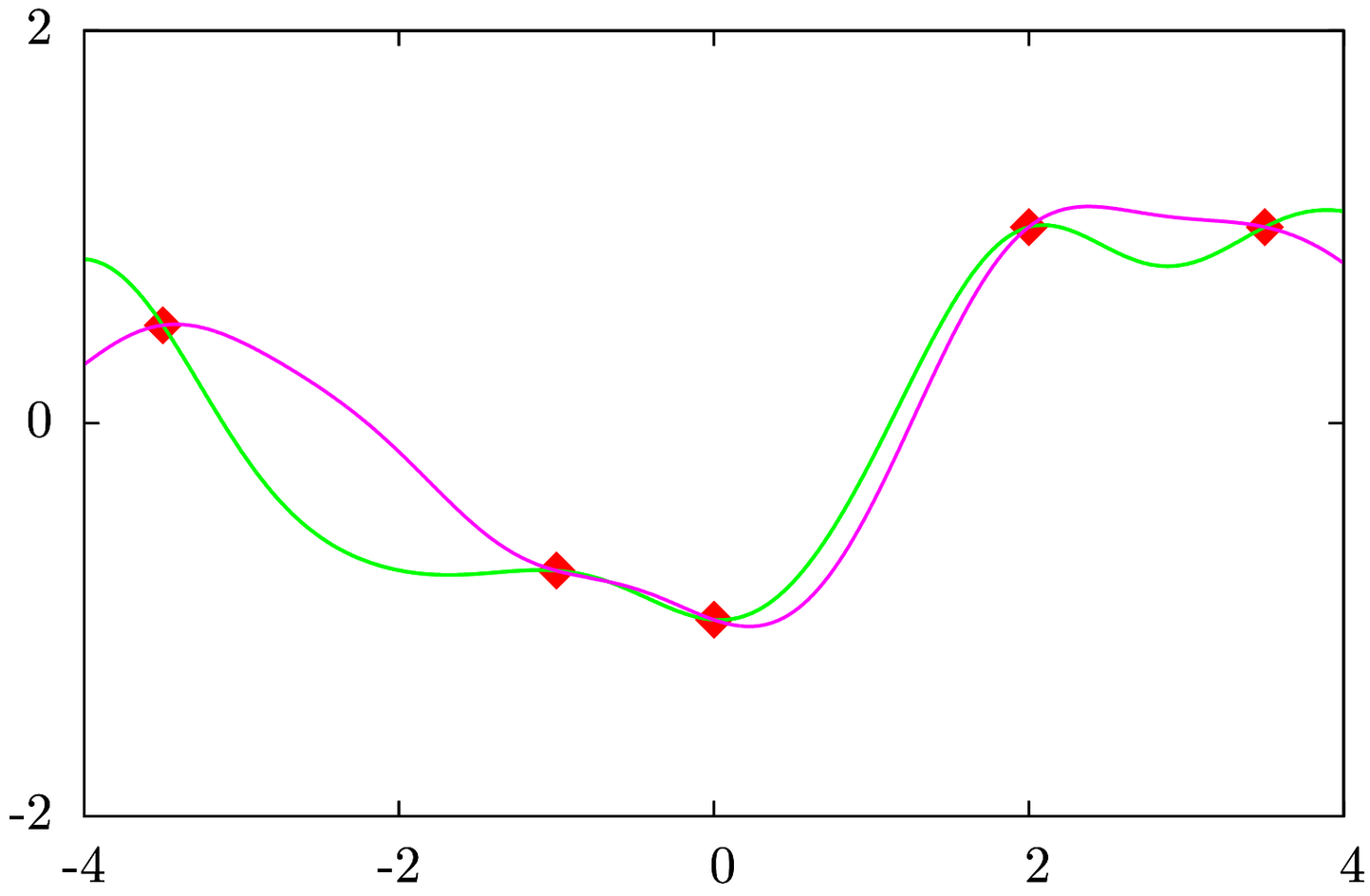

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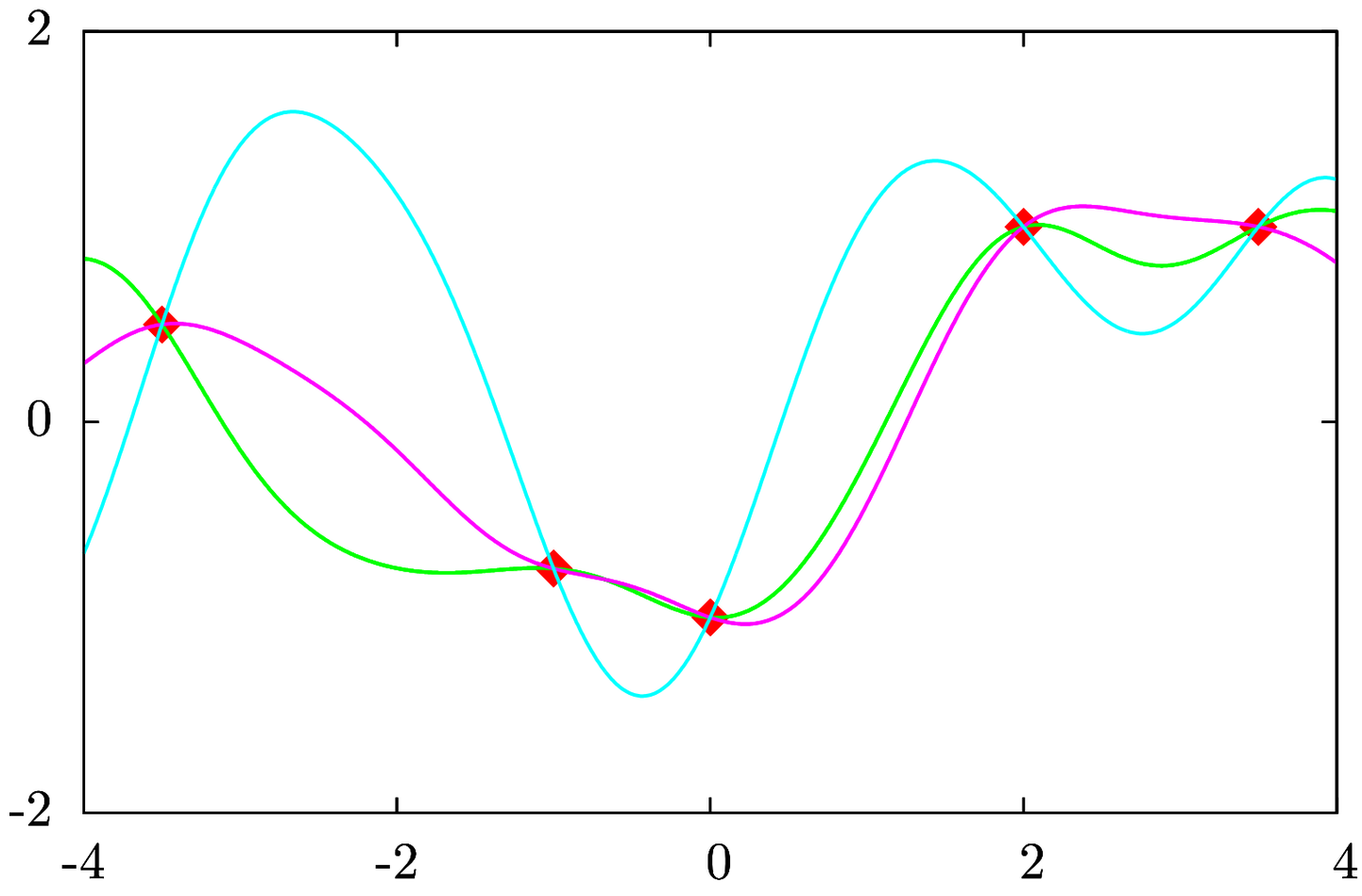

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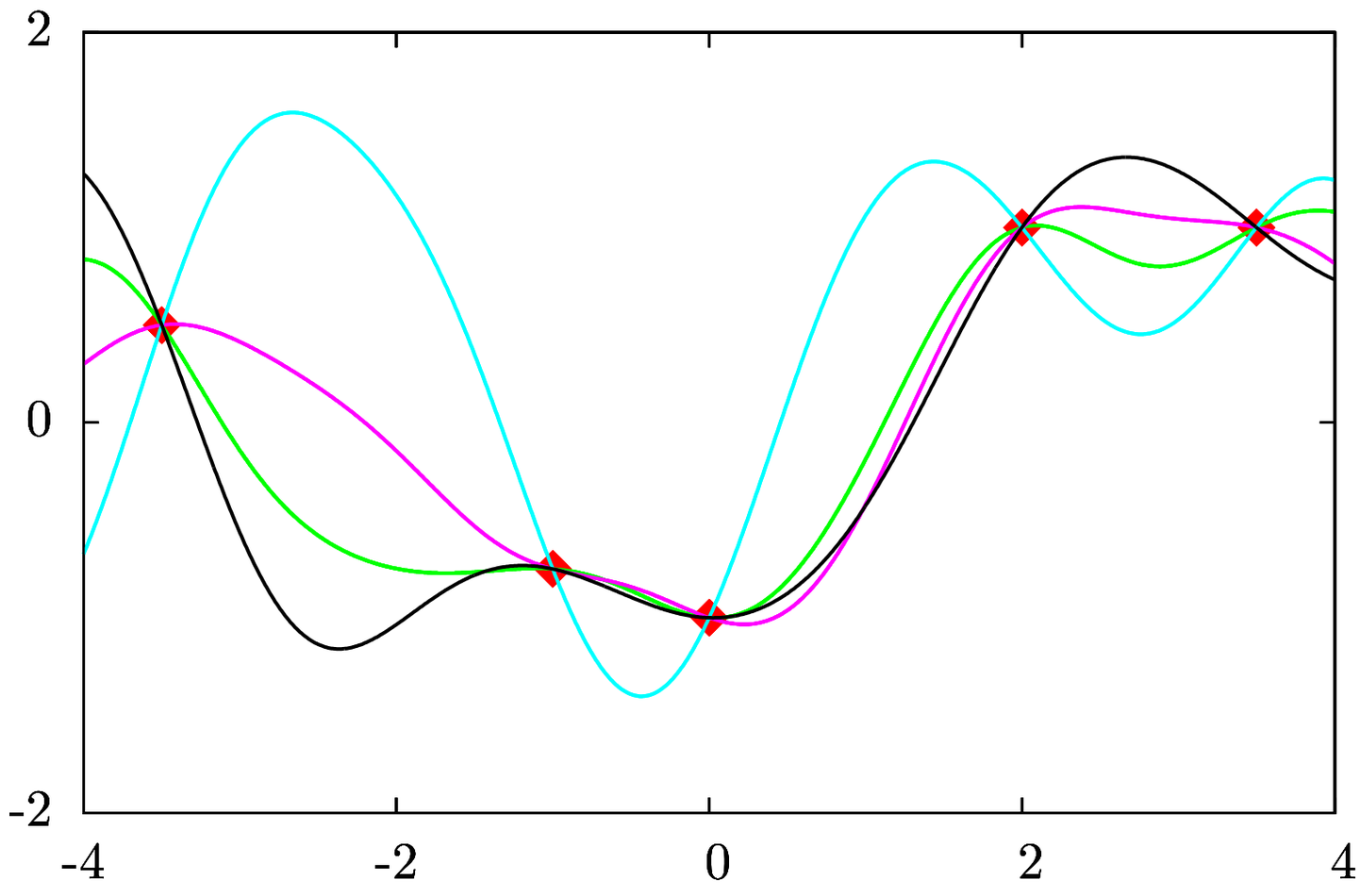

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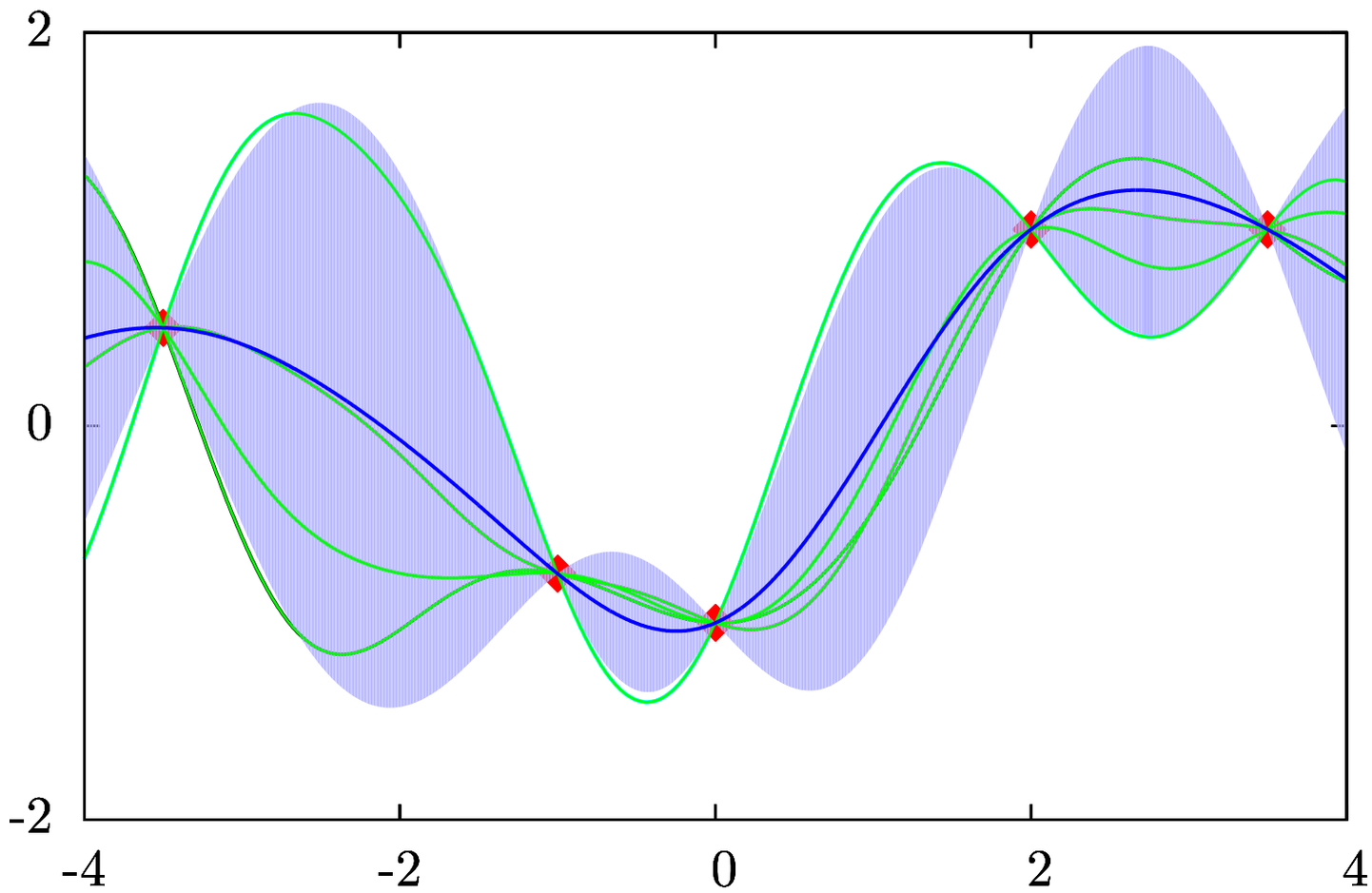

Generalised input data

- Often direct measurements of $\mathbf{y}_i$ not available
- Consider any linear operator $L(\mathbf{y})$
  Compute $P(y_{N+1}|L(\mathbf{y}))$

  L can be built using Σ , $\partial/\partial x$ etc
- Basis functions adapt to input data, e.g. $\partial k(x, x')/\partial x$ for derivative data
- Can deal with gradient data, sums, etc.

Traditional ideas for functional forms

- Pair potentials: Lennard-Jones, RDF-derived, etc.
- Three-body terms: Stillinger-Weber, MEAM, etc.
- Embedded Atom (no angular dependence)
- Bond Order Potential (BOP)

  Tight-binding-derived attractive term with pair-potential repulsion
- ReaxFF: kitchen-sink + hundreds of parameters

$$\varepsilon_i = \frac{1}{2}\sum_j V_2(|r_{ij}|) + \sum_{jk} k(\theta_{ijk} - \theta_0)^2$$

$$\varepsilon_i = \Phi\left(\textstyle\sum_j \rho(|r_{ij}|)\right)$$

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Limited accuracy, not systematic

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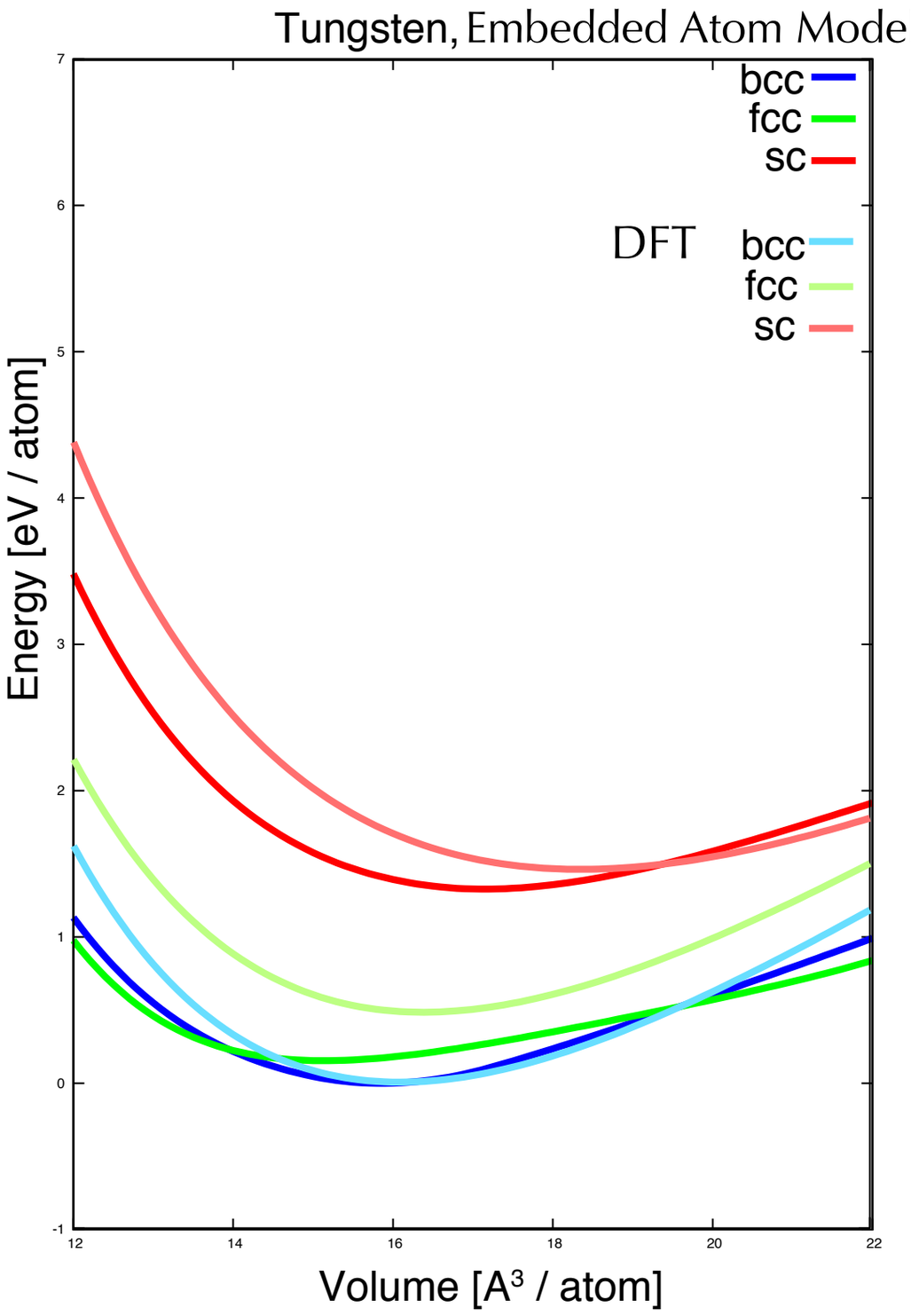
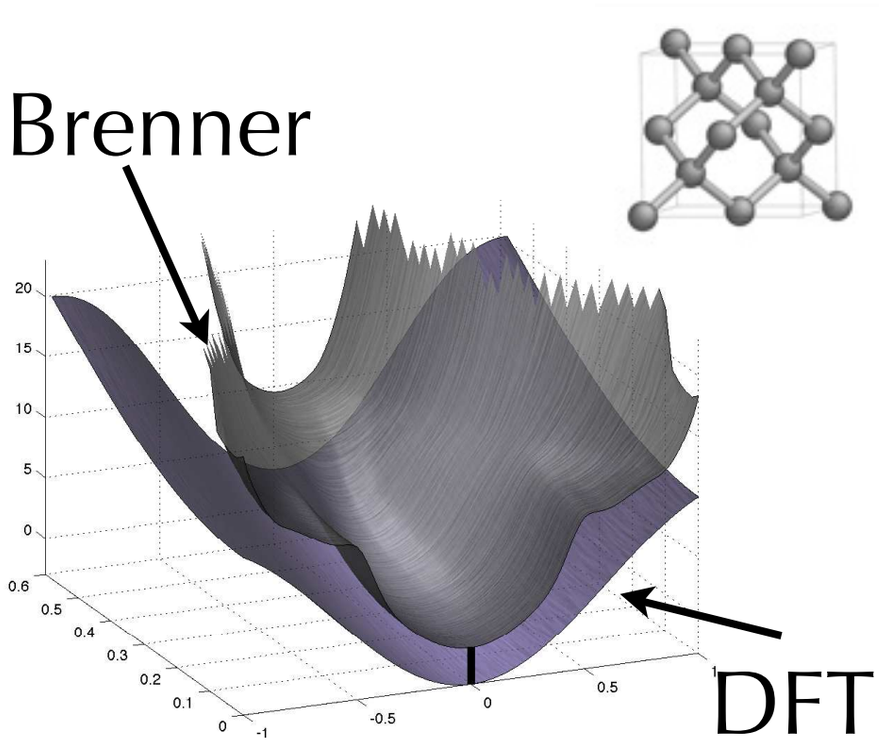
given by

GOAL: potentials ~~based on~~ quantum mechanics

Fundamental limitation of analytic functional form



Carbon (diamond)

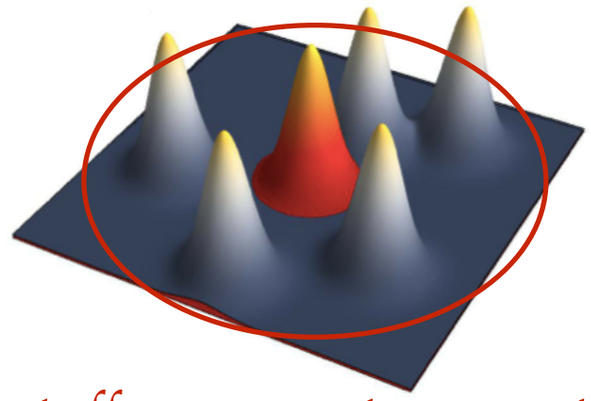


Elastic constants:

	DFT	Brenner
C_{11}	1118	1061
C_{12}	151	133
C_{44}^0	610	736
C_{44}	603	717

Construct smooth similarity kernel directly

$$\rho_i(\mathbf{r}) = \sum_j \exp\left(-|\mathbf{r} - \mathbf{r}_{ij}|^2/2\sigma^2\right) = \sum_j \sum_{lm} c_{nlm}^{(i)j} g_n(r) Y_{lm}(\hat{\mathbf{r}})$$



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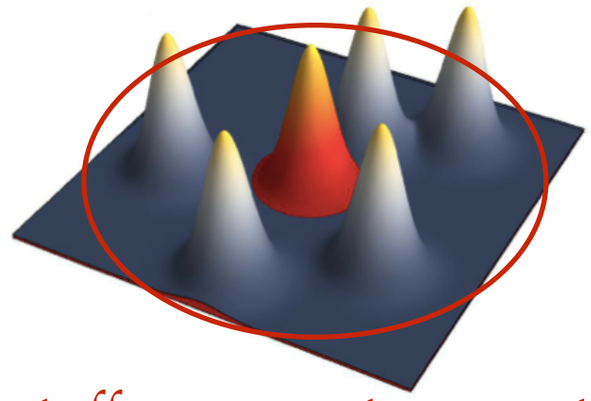
- Overlap integral

$$S(\rho_i, \rho_{i'}) = \int \rho_i(\mathbf{r})\rho_{i'}(\mathbf{r})d\mathbf{r},$$



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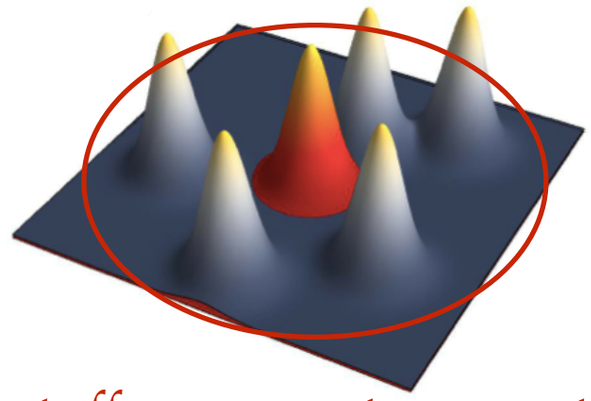

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- Integrate over all 3D rotations:

$$k(\rho_i, \rho_{i'}) = \int \left| S(\rho_i, \hat{R}\rho_{i'}) \right|^2 d\hat{R} = \int d\hat{R} \left| \int \rho_i(\mathbf{r}) \rho_{i'}(\hat{R}\mathbf{r}) d\mathbf{r} \right|^2$$

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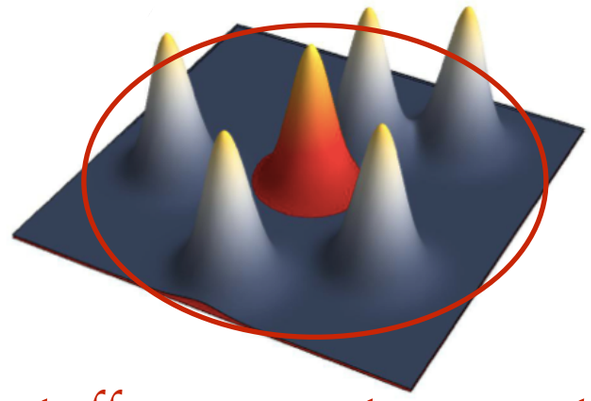

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- After LOTS of algebra: SOAP kernel

$$k(\rho_i, \rho_{i'}) = \sum_{n,n',l} p_{nn'l}^{(i)} p_{nn'l}^{(i')} \qquad p_{nn'l} = \mathbf{c}_{nl}^{\dagger}\mathbf{c}_{n'l}$$

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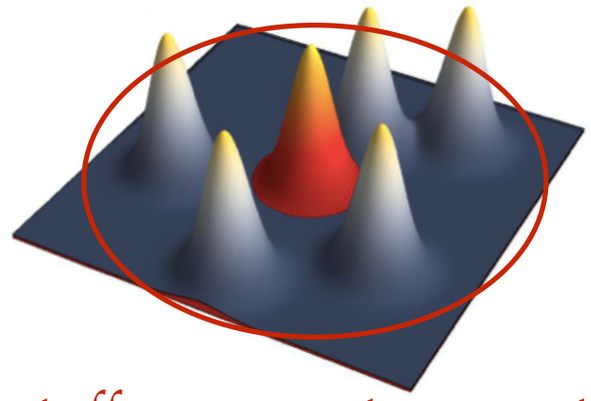

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$$\boxed{K(\mathbf{q}, \mathbf{q}') \propto |k(\rho, \rho')|^{\xi}}$$

How to generate databases?

- Target applications: large systems
- Capability of full quantum mechanics (QM): small systems

QM MD on "representative" small systems:

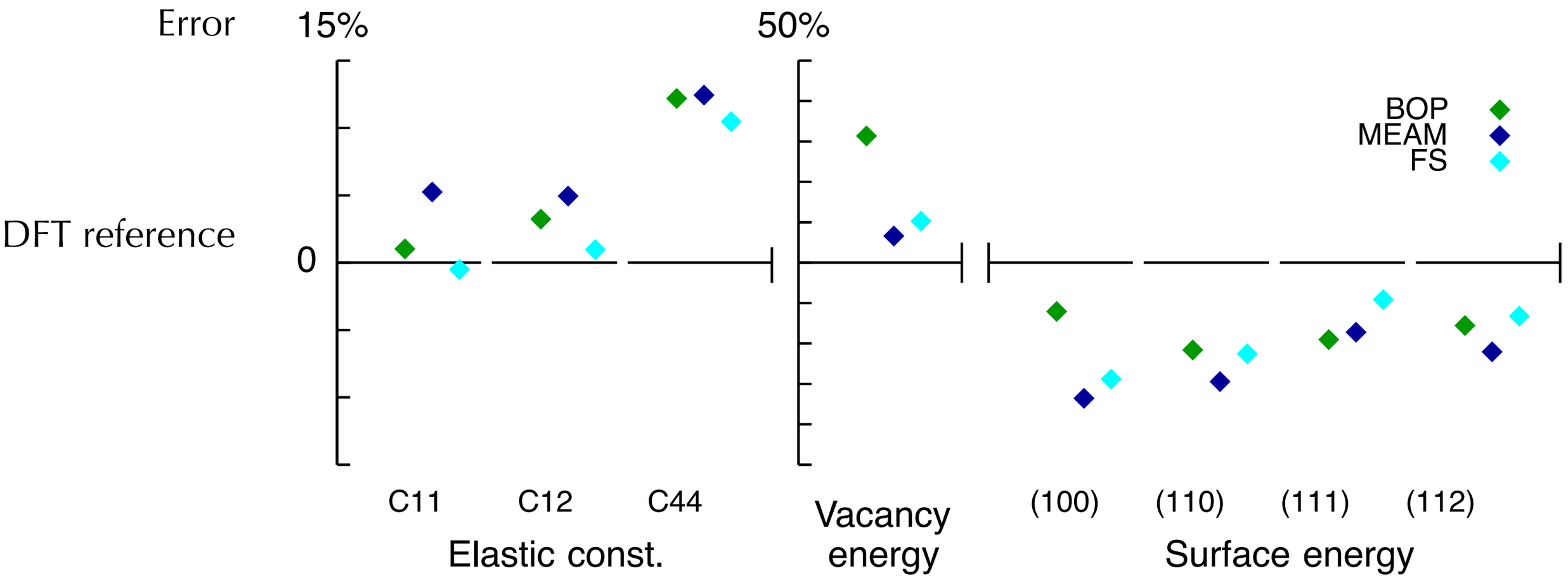
sheared primitive cell → elasticity
large unit cell → phonons
surface unit cells → surface energy
gamma surfaces → screw dislocation
vacancy in small cell → vacancy
vacancy @ gamma surface → vacancy near dislocation

Iterative refinement

1. QM MD → Initial database
2. Model MD
3. QM → Revised database

What is the acceptable validation protocol?
How far can the domain of validity be extended?

Existing potentials for tungsten



DFT code	CASTEP [37] (version 6.01)
Exchange-correlation functional	PBE
Pseudopotential	Ultrasoft (valence $5s^2 5p^6 5d^4 6s^2$)
Plane-wave energy cutoff	600 eV
Maximum k-point spacing	0.015 $Å^{-1}$
Electronic smearing scheme	Gaussian
Smearing width	0.1 eV

Building up databases for tungsten (W)

	Database:	Computational cost[a] [ms/atom]	Elastic constants[b] [GPa]	Phonon spectrum[b] [THz]	Vacancy formation[c] [eV]	Surface energy[b] [eV/Å^2]	Dislocation structure[d] [Å^{-1}]	Dislocation-vacancy binding energy [eV]	Peierls barrier [eV/b]
GAP_1 :	2000 × primitive unit cell with varying lattice vectors	24.70	0.623	*0.583*	*2.855*	*0.1452*	*0.0008*		
GAP_2 :	GAP_1 + 60 × 128 atom cell	51.05	0.608	0.146	*1.414*	*0.1522*	*0.0006*		
GAP_3 :	GAP_2 + vacancy in: 400 × 53 atom cell, 20 × 127 atom cell	63.65	0.716	0.142	0.018	*0.0941*	*0.0004*		
GAP_4 :	GAP_3 + (100), (110), (111), (112) surfaces 180 × 12 atom cell; (110), (112) gamma surfaces 6183 × 12 atom cell	86.99	0.581	0.138	0.005	0.0001	0.0002	*-0.960*	*0.108*
GAP_5 :	GAP_4 + vacancy in: (110), (112) gamma surface 750 × 47 atom cell	93.86	0.865	0.126	0.011	0.0001	0.0002	-0.774	*0.154*
GAP_6 :	GAP_5 + $\frac{1}{2}\langle 111\rangle$ dislocation quadrupole 100 × 135 atom cell	93.33	0.748	0.129	0.015	0.0001	0.0001	-0.794	0.112

[a] Time on a single CPU core of Intel Xeon E5-2670 2.6GHz, [b] RMS error, [c] formation energy error, [d] RMS error of Nye tensor over the 12 atoms nearest the dislocation core, cf. Figure 2.

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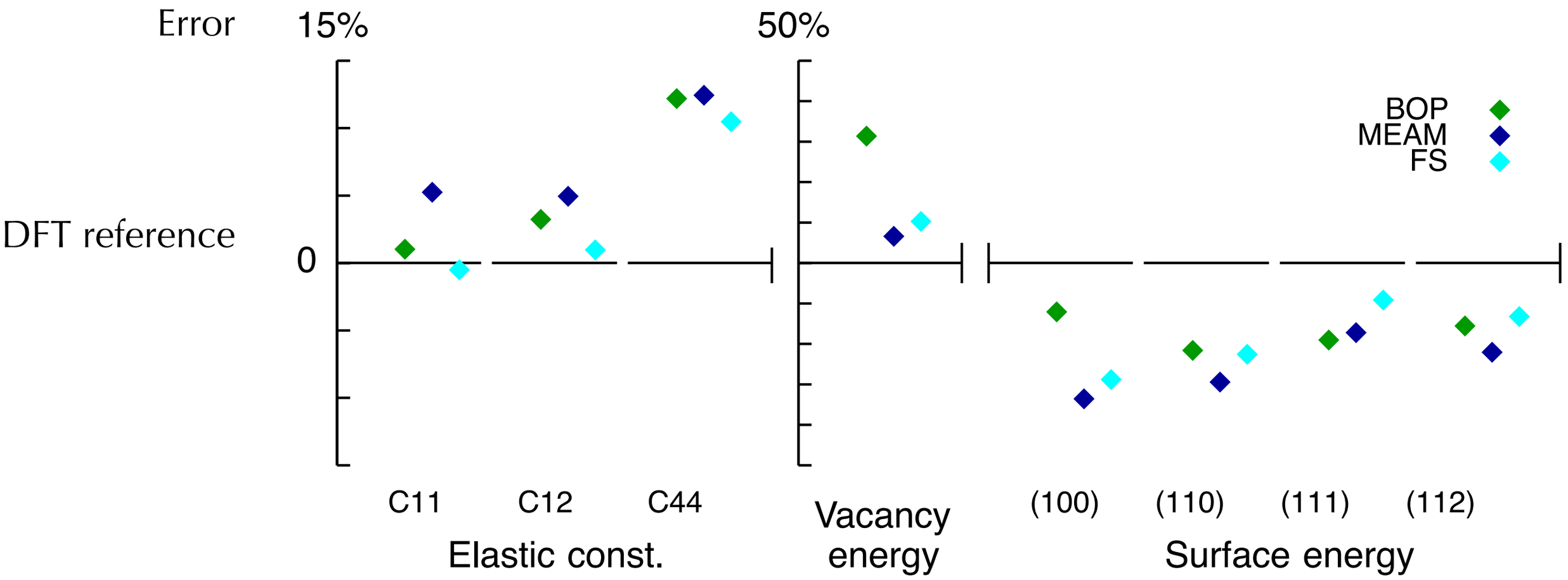

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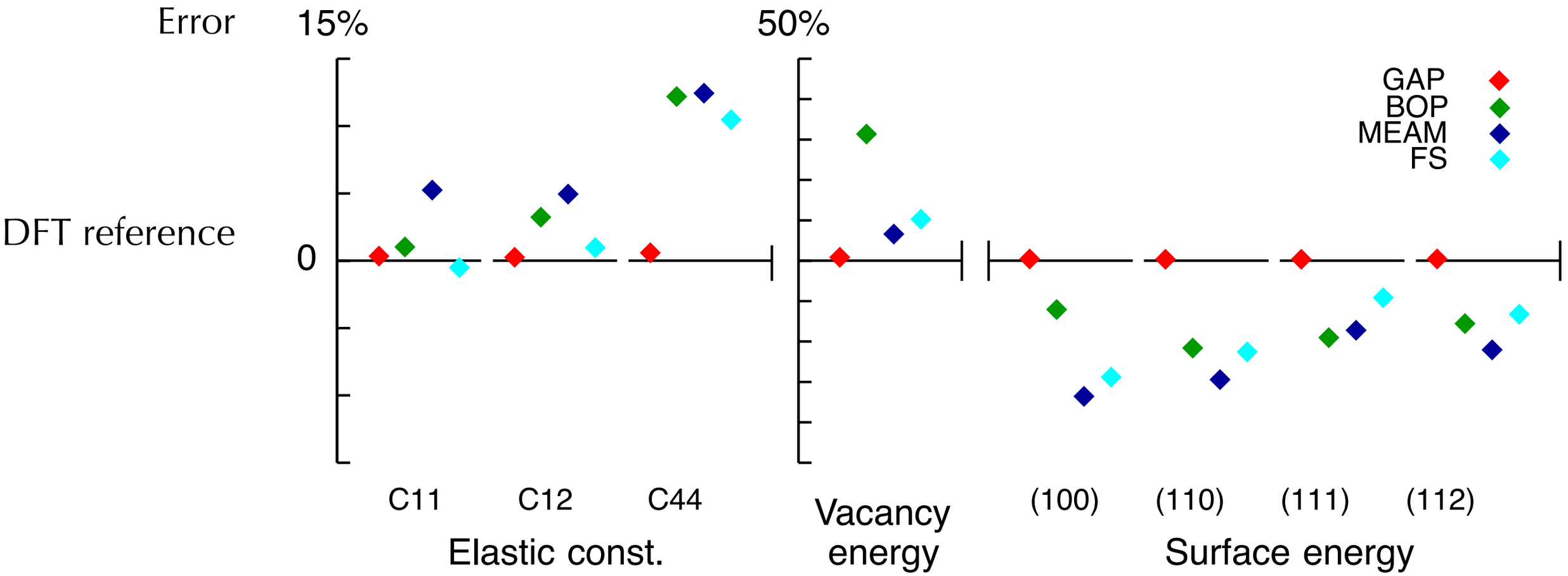
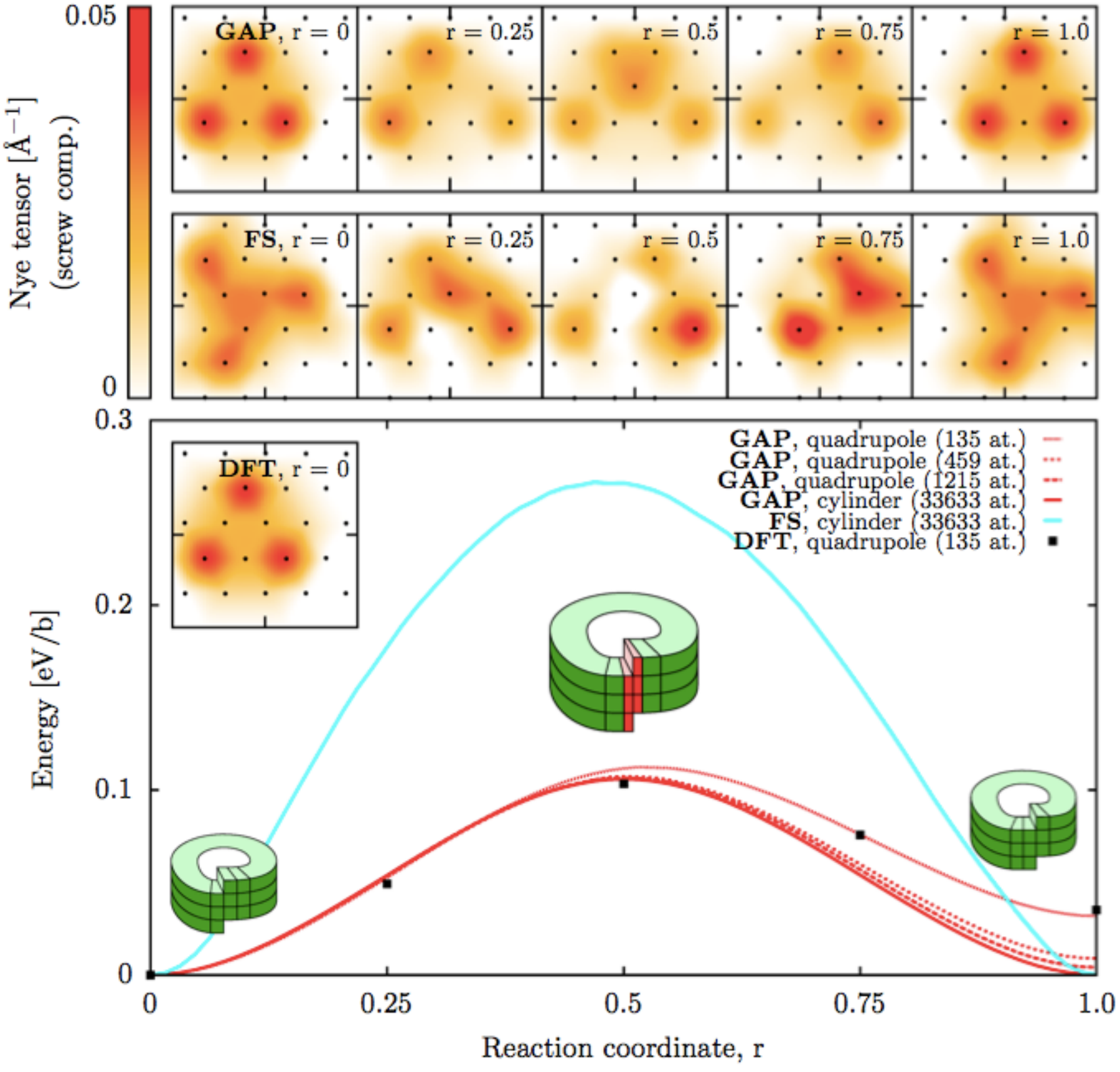
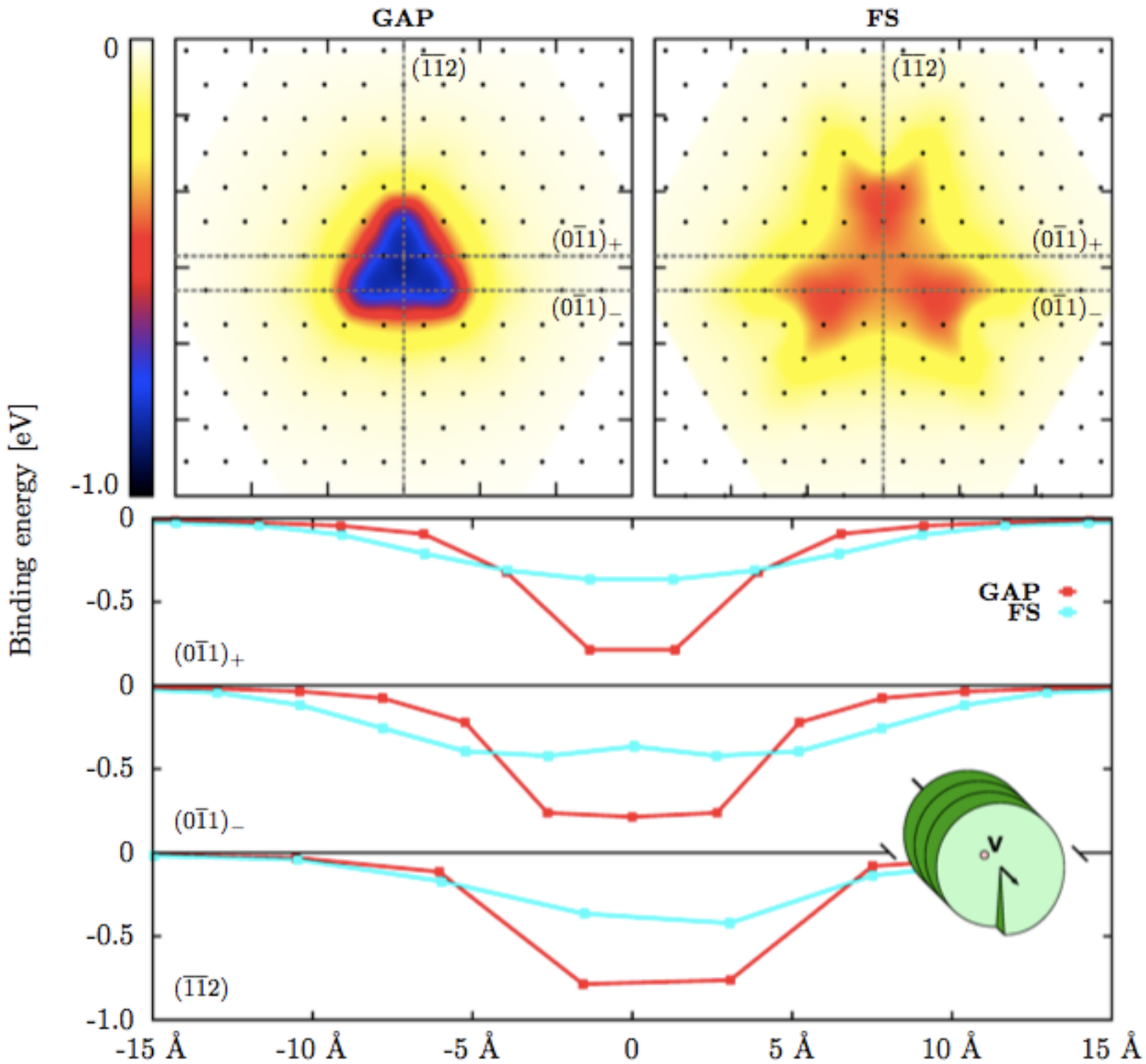


Peierls barrier for screw dislocation glide



Vacancy-dislocation binding energy

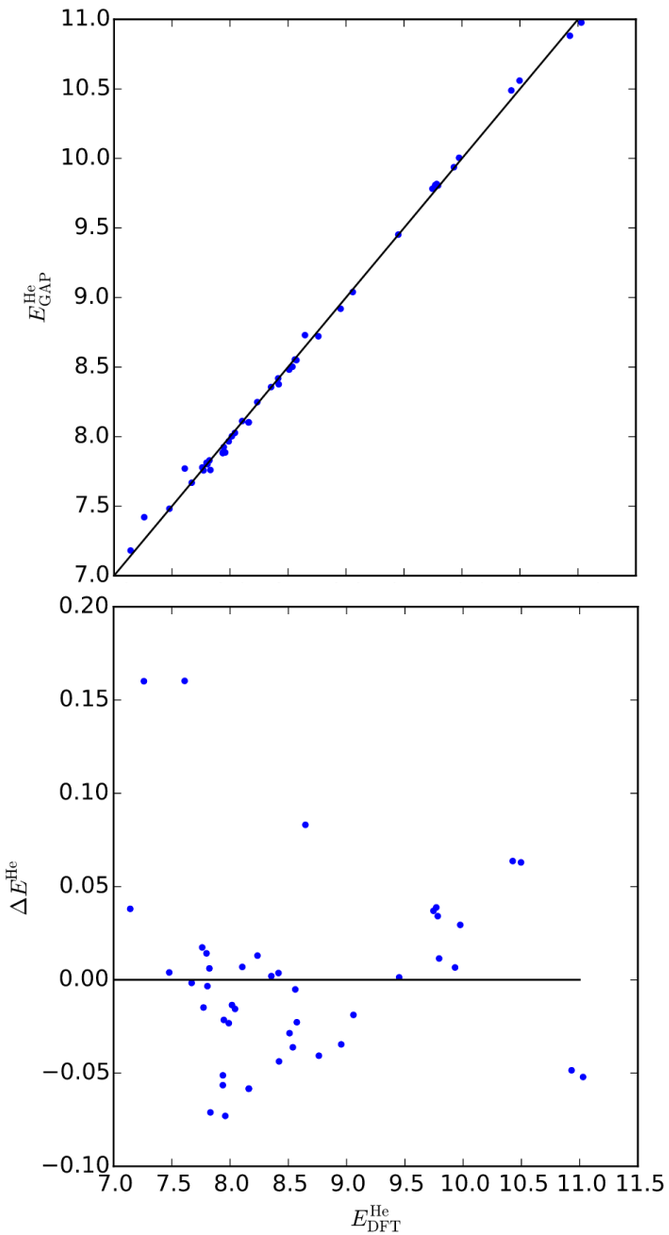


(~100,000 atoms in 3D simulation box)

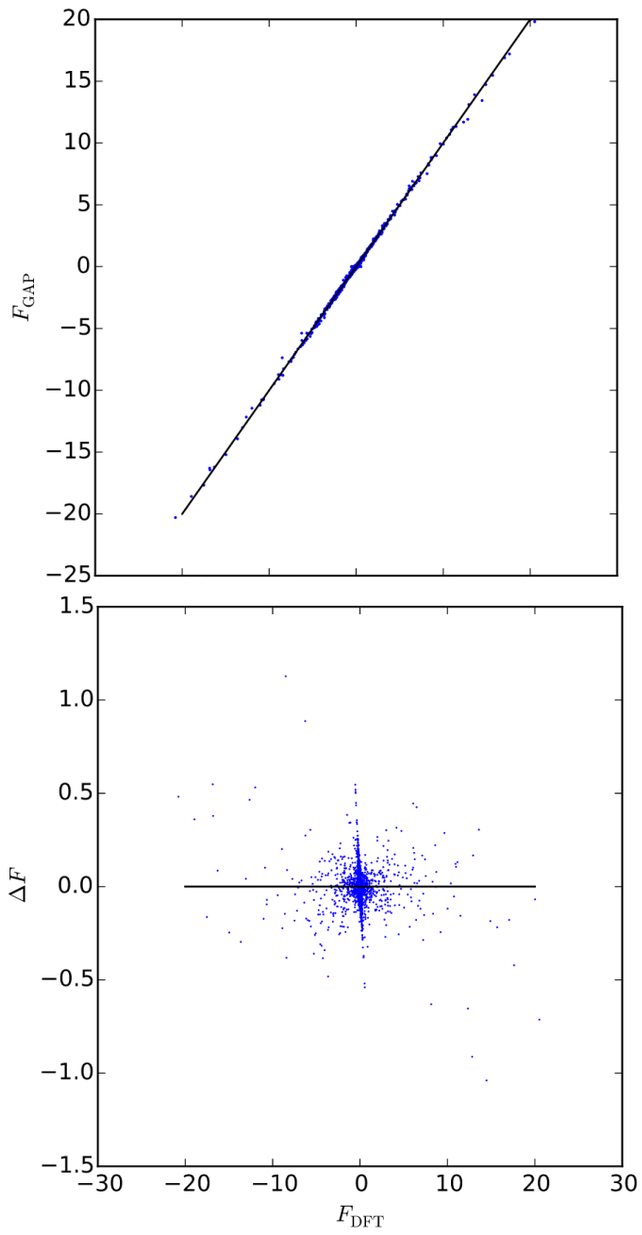
He-Vacancy interaction in tungsten - preliminary

- Collaboration with Duc Nguyen-Manh (CCFE)
- Add He-W interaction on top of W potential
- 200 training configurations of He@V, 44 test

energy error

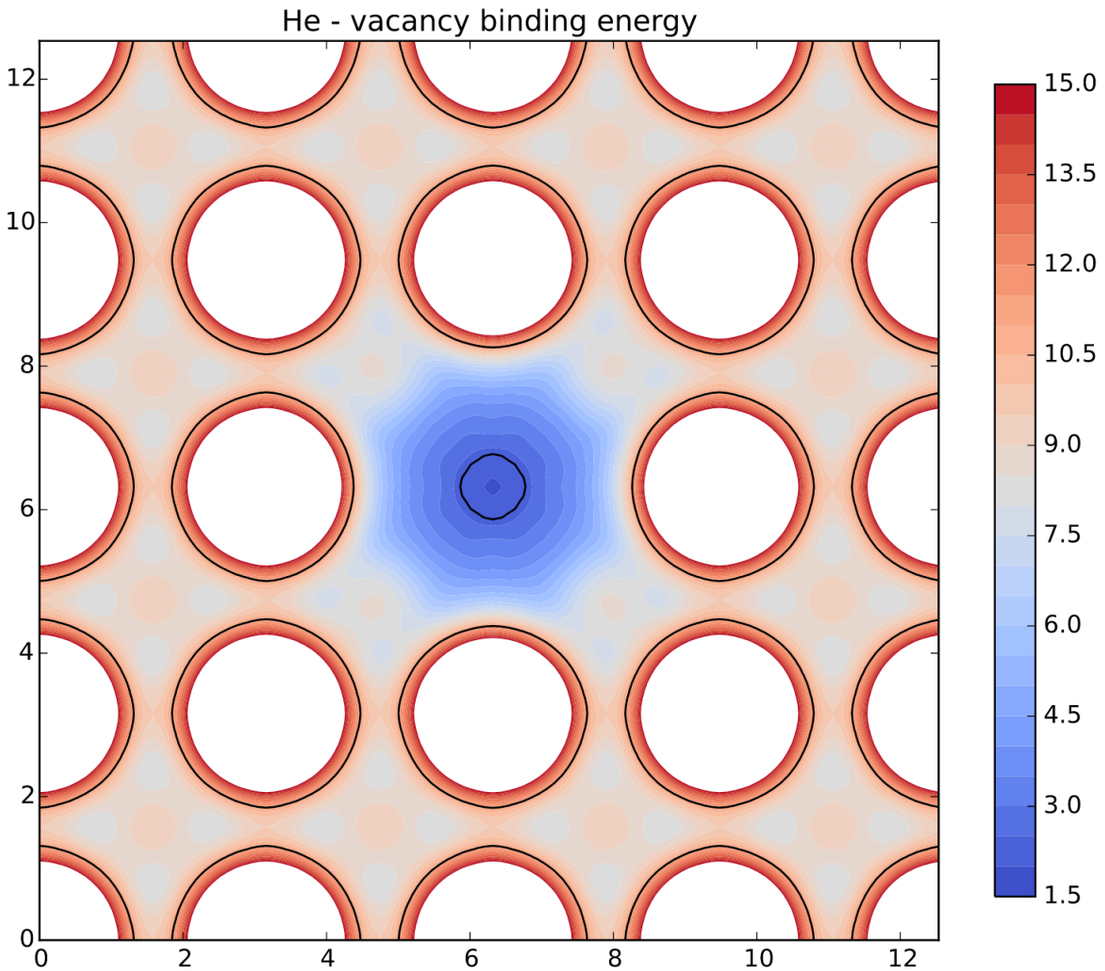


force error

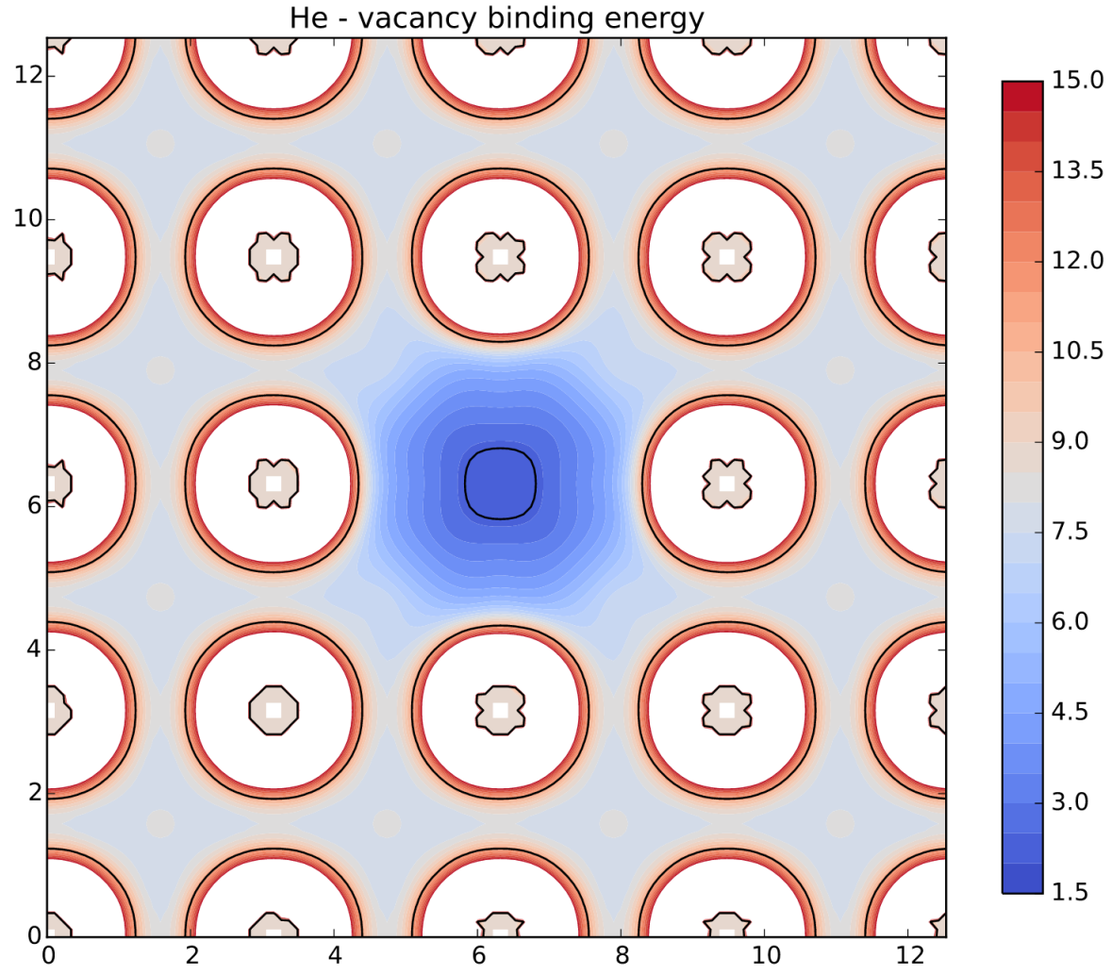


He-Vacancy interaction in tungsten

2-body



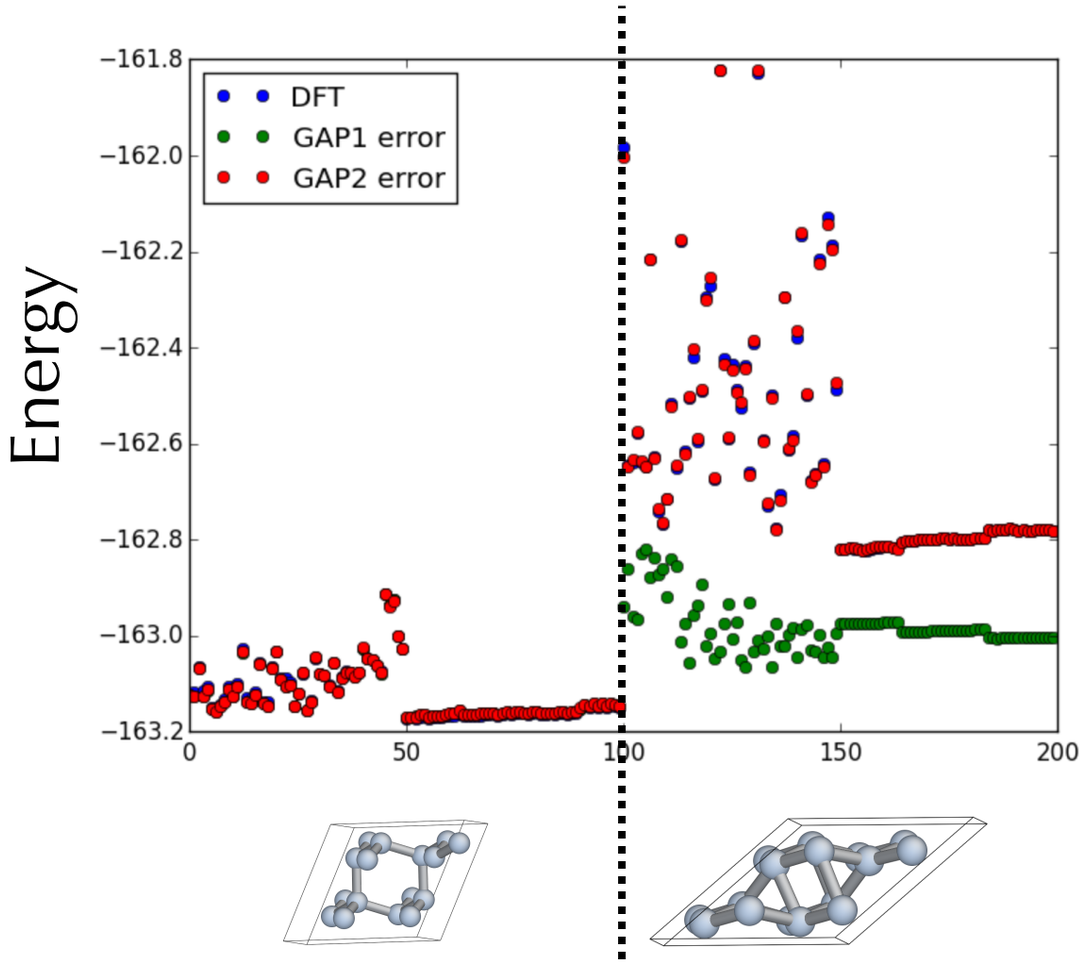
SOAP-GAP

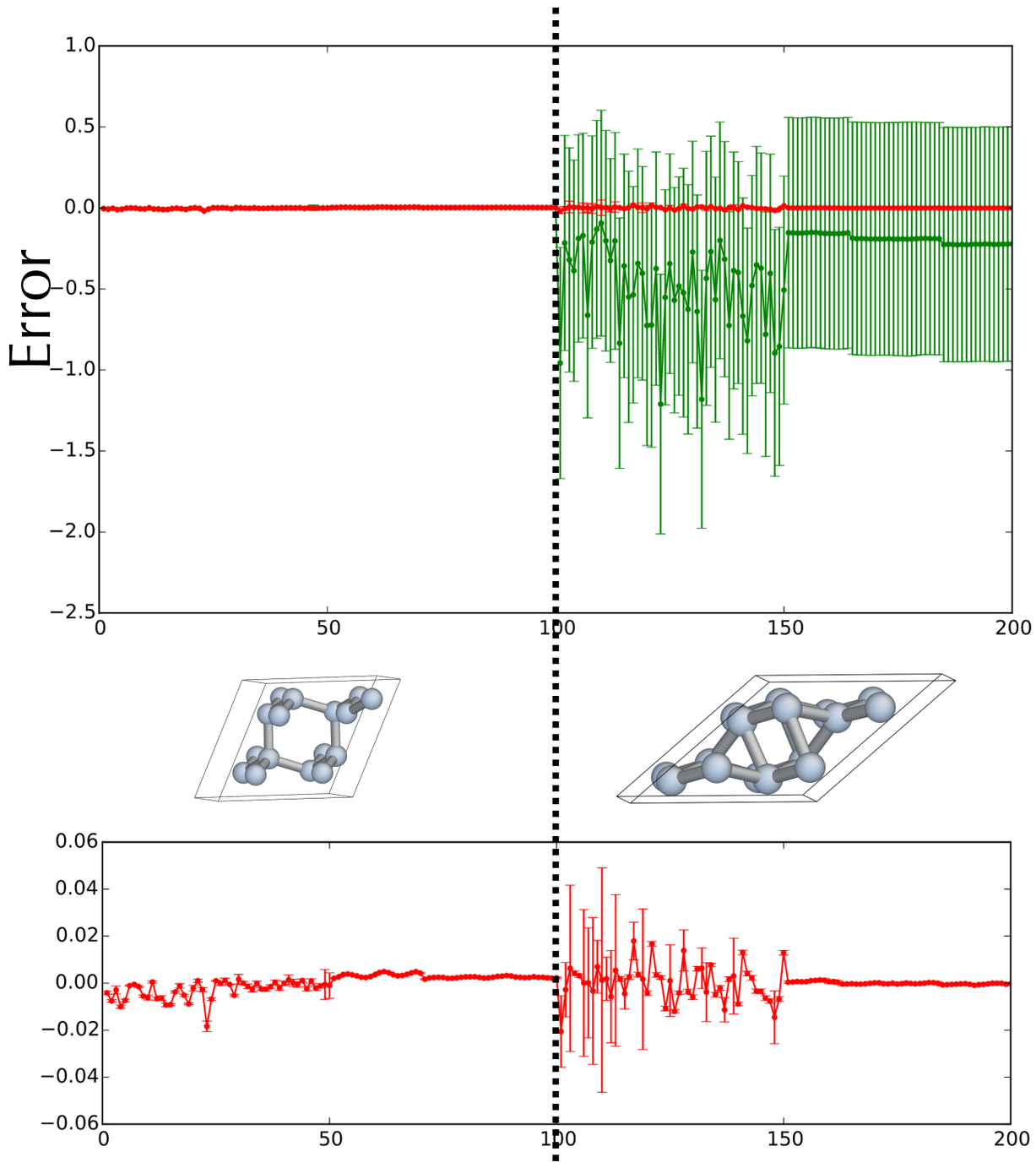


- Needs more He data, other defects
- Do the same with H@W, with Takuji Oda

Self-aware potentials: predicting the error

- Bulk silicon: Diamond and Beta-tin phases
- Predicted error correctly signals where GAP is unreliable





Outstanding problems

- Accuracy on database ⟶ accuracy in properties?
- Database contents ⟶ region of validity ?
- Alloys - permutational complexity? Chemical variability?
- Systematic treatment of long range effects
- Electronic temperature