The Cambrian Explosion of Machine Learning Potentials

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Chemical Sciences and Sustainability
Research Alliance Ruhr

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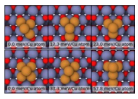
Introduction

Goal:

Atomic-level understanding of complex systems in chemistry and materials science

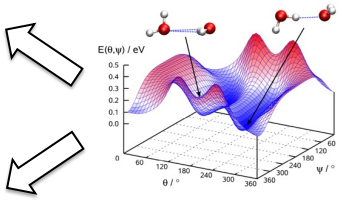
⇒ Predictive computer simulations with first-principles quality

Energy
global and local minima

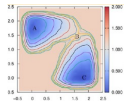


Forces
dynamics, free energies

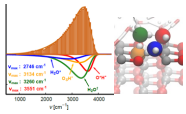
Central Role:
Potential Energy Surface



Reactions
barriers / transition states



Vibrations
properties, analysis



⇒ The accuracy of the obtained results depends on the quality of the PES

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Definition of Machine Learning Potentials

RUB

There is no universally accepted definition of machine learning potentials

Challenge: The construction essentially all atomistic potentials involves fitting/parameter optimization.

⇒ Where is the border between fitted potentials and MLPs?

A pragmatic definition of Machine Learning Potentials

- A machine learning potential uses a flexible machine learning method to represent the potential energy surface (total energy and its analytic derivatives) as a function of the atomic coordinates.

  ⇒ in principle no physical functional form needed
- A machine learning potential is constructed using a consistent set of reference electronic structure calculations.

⇒ No "artificial intelligence", just brute force fitting (?)

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The Cambrian Explosion of Machine Learning Potentials: Reasons

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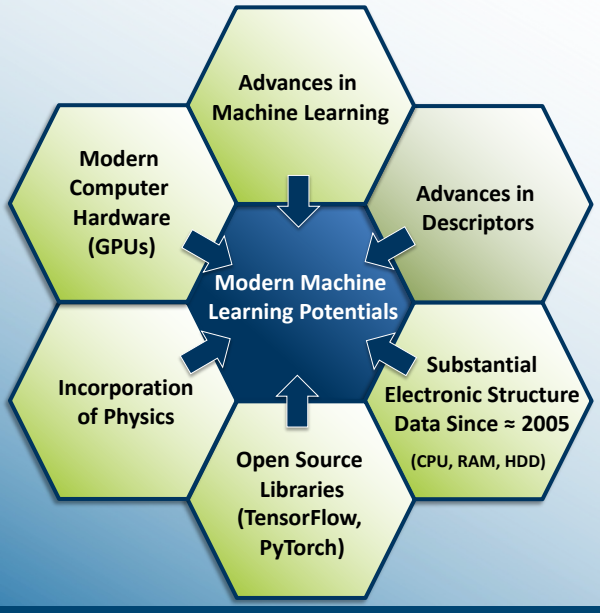

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The Cambrian Explosion of Machine Learning Potentials

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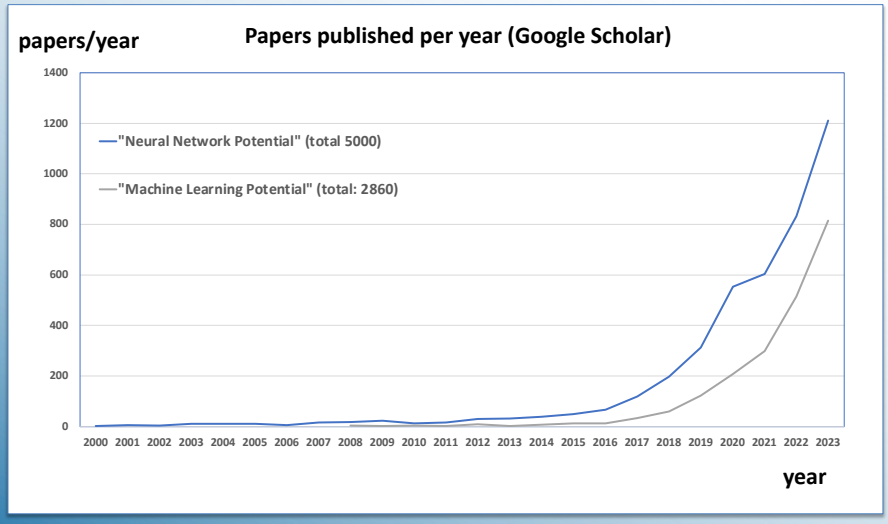

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Machine Learning Potentials

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How to get an overview about the huge amount of papers?

We need a classification scheme for machine learning potentials
What are the criteria?

Historical?

Physics?

Applicability?

ML Method?

Descriptors?

⇒ There is no unique way

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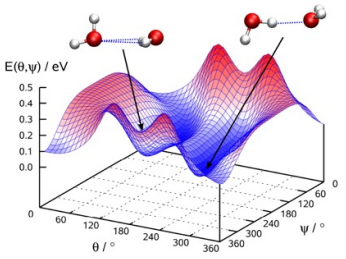
First-Generation Machine Learning Potentials 1995 – 2007



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Machine Learning Potentials

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1995 2000 2005 2010 2015 2020

First-Generation MLPs

- about 30 papers (1995 – 2007) from about 10 groups
- all methods in the first decade are based on neural networks

Examples:

T.B. Blank, S.D. Brown, A.W. Calhoun, and D.J. Doren, *J. Chem. Phys.* **103** (1995) 4129.
H. Gassner, M. Probst, A. Lauenstein, K. Hermansson, J. Phys. Chem. A **102** (1998) 4596.
S. Lorenz, A. Groß, M. Scheffler, Chem. Phys. Lett. **395** (2004) 210.
S. Manzhos, T. Carrington, Jr., J. Chem. Phys. **125** (2006) 194105.
J. Behler, S. Lorenz, K. Reuter, J. Chem. Phys. **127** (2007) 014705.

Focus:

Training
Symmetry
Surfaces
Spectroscopy
Surface Symmetry

⇒ **Basic ideas and key concepts are well established**

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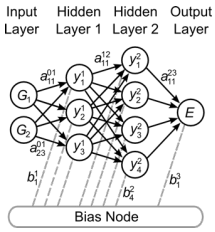
Machine Learning Potentials

RUB

1995 2000 2005 2010 2015 2020

First-Generation MLPs

Limitation: Applicable to low-dimensional systems only

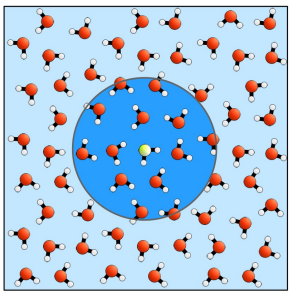


Challenges:

- limited number of dimensions (up to ≈ 12)
- permutation symmetry of the system not included (change in order of atoms changes the energy)
- energy depends on rotation and translation
- potential is valid only for a given system size (number of atoms)

⇒ **Another approach is required for high-dimensional systems**

Second-Generation Machine Learning Potentials: Locality



High-Dimensional Neural Network Potentials

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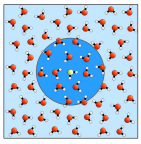
3 Steps:

1. Total energy is the sum of atomic energies

$$E = \sum_i E_i$$

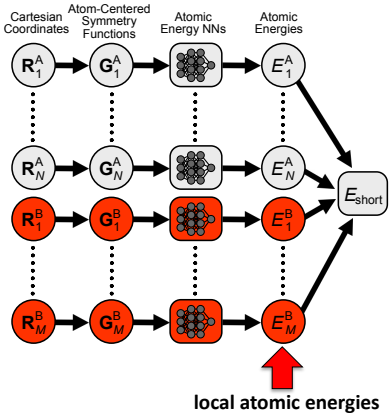
2. Atomic energies depend on local environments
   ⇒ cutoff radius



3. Description of local atomic environments by many-body atom-centered symmetry functions
   ⇒ structural fingerprints
   (invariances: rotation, translation, permutation)

J. Behler, M. Parrinello, *Phys. Rev. Lett.* 98 (2007) 146401.
J. Behler, *J. Chem. Phys.* 134 (2011) 074106.
J. Behler, *Angew. Chem. Int. Ed.* 56 (2017) 12828.

Structure for a binary system A_NB_M



⇒ applicable to thousands of atoms

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Second-Generation Machine Learning Potentials

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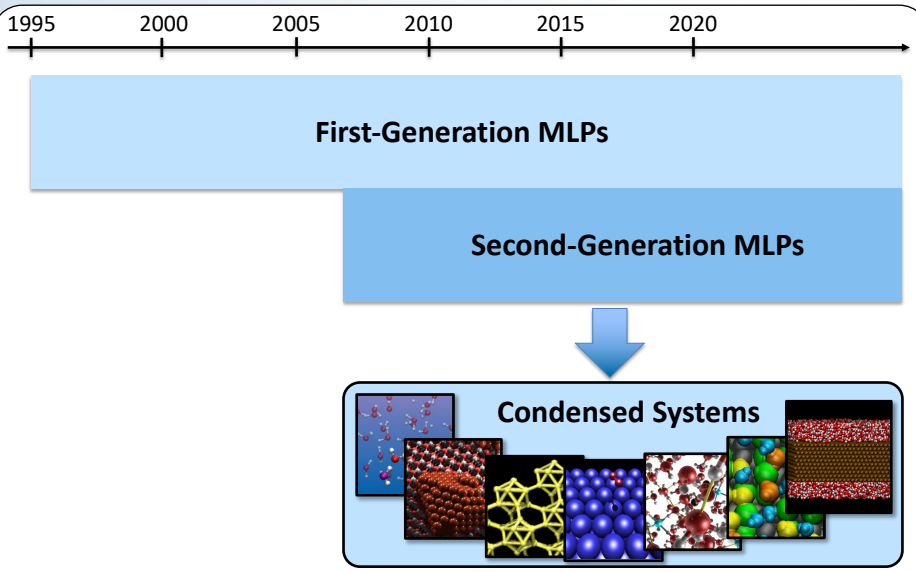

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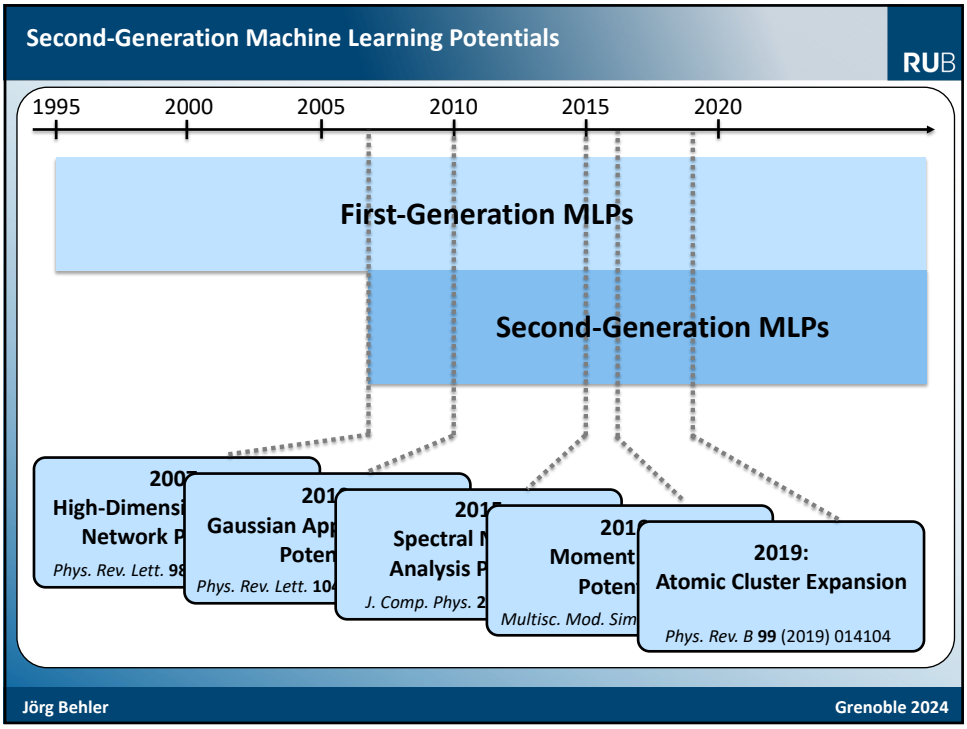
Second-Generation Machine Learning Potentials
RUB
1995
2000
2005
2010
2015
2020
First-Generation MLPs
Second-Generation MLPs
2019:
Atomic Cluster Expansion
Phys. Rev. B 99 (2019) 014104
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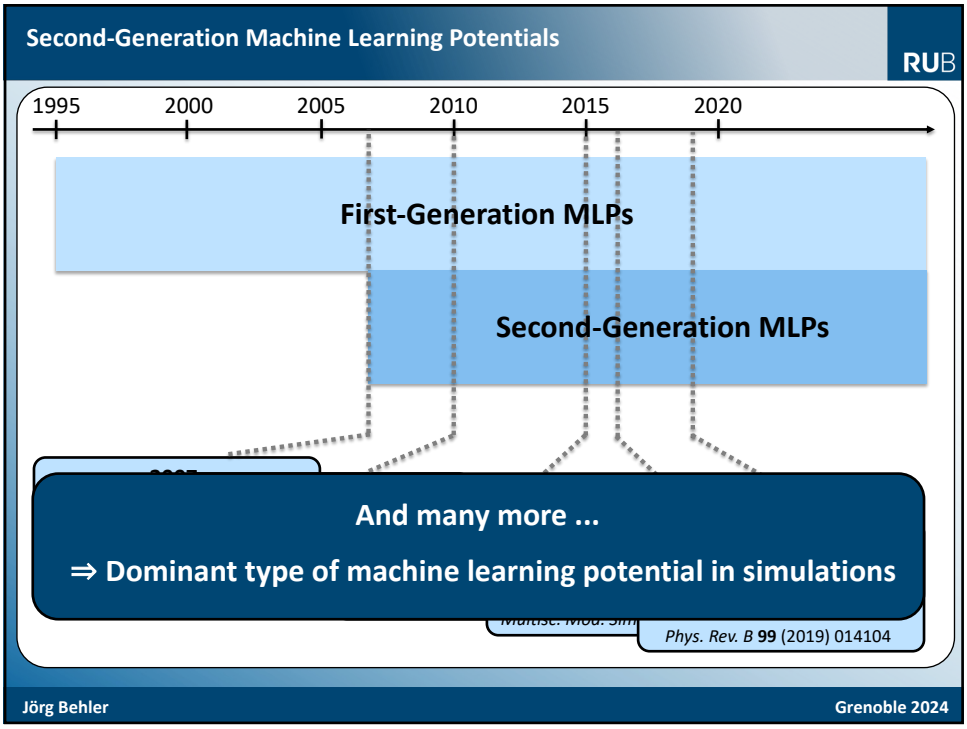
Second-Generation Machine Learning Potentials
RUB
1995
2000
2005
2010
2015
2020
First-Generation MLPs
Second-Generation MLPs
And many more ...
⇒ Dominant type of machine learning potential in simulations
Phys. Rev. B 99 (2019) 014104
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Grenoble 2024

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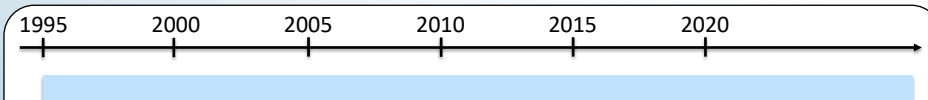
Second-Generation Machine Learning Potentials

RUB



First-Generation MLPs

Second-Generation MLPs

Limitation: Truncation of the interactions at the cutoff radius

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Hessian-based Locality Test

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A Hessian-Based Analytic Locality Test

Challenge: Atomic forces depend on the entire environment

- different neighbors interact differently
  ⇒ distance and type of bonding are important
  ⇒ ***influence of individual neighbors*** is of interest
- forces are very small or even zero in symmetric environments
  ⇒ ***forces are not a good measure*** for interaction strength
- force convergence of central atom measures only total interaction
  ⇒ ***forces can cancel each other*** also in non-symmetric environments

Solution:

Hessian: $H_{A_\alpha B_\beta} = \frac{\partial^2 E}{\partial A_\alpha \partial B_\beta} = -\frac{\partial f_{B_\beta}}{\partial A_\alpha} = -\frac{\partial f_{A_\alpha}}{\partial B_\beta}$ with $\alpha, \beta = \{x, y, z\}$

⇒ information about dependence of an atomic force on each atom in the system

⇒ spatial cutoff can be quantified!

M. Herbold and J. Behler, J. Chem. Phys. **156** (2022) 114106.

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Hessian-based Locality Test

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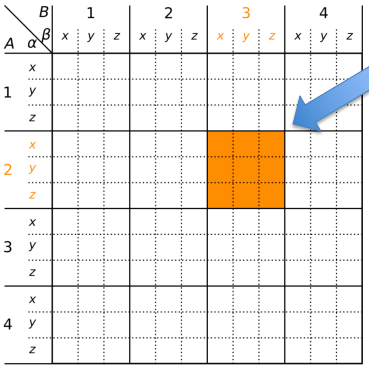
DFT Hessian: $H_{A_\alpha B_\beta} = \frac{\partial^2 E}{\partial A_\alpha \partial B_\beta} = -\frac{\partial f_{B_\beta}}{\partial A_\alpha} = -\frac{\partial f_{A_\alpha}}{\partial B_\beta}$ with $\alpha, \beta = \{x, y, z\}$

Hessian: (3*N* x 3*N*) matrix



Dependence of atomic force vector on atomic position of a neighbor: (3x3) matrix

⇒ inconvenient, scalar property needed

⇒ Hessian submatrix norm

$$||\mathbf{h}_{AB}|| = \sqrt{\sum_{\alpha=x,y,z} \sum_{\beta=x,y,z} h^2_{A_\alpha B_\beta}}$$

Dependence of force on each individual atom in the system can be quantified

M. Herbold and J. Behler, J. Chem. Phys. **156** (2022) 114106.

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Hessian-based Locality Test

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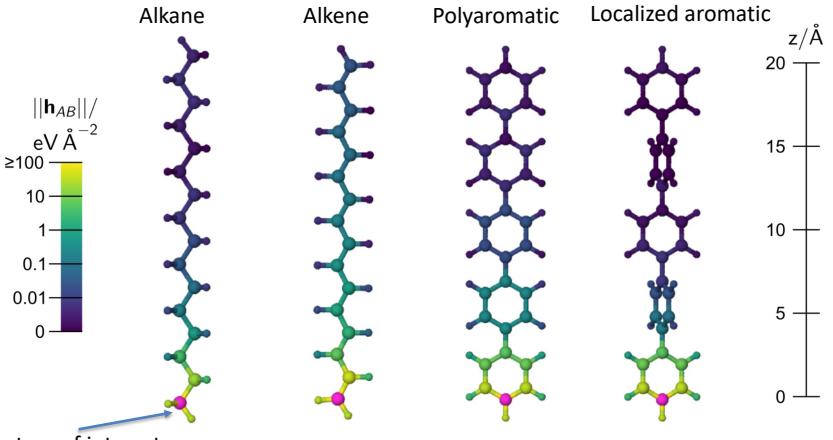
1D Model Systems



atom of interest: terminal **carbon**

- contribution of each atom in the system can be quantified
- no cancellation of contributions possible

M. Herbold and J. Behler, J. Chem. Phys. **156** (2022) 114106.

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Second-Generation Machine Learning Potentials

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2G MLPs are the main production methods for MLP-driven simulations

There are now two classes:

Predefined Descriptors (HDNNP, SOAP, DeePMD,...)

- simple ⇒ fast
- most applications so far
- more difficult for many elements

Message Passing Neural Networks (DTNN, SchNet, MACE, ...)

- iterative extension of environment
- learnable features
  ⇒ more demanding

⇒ for a given system the accuracy is very similar

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Second-Generation Machine Learning Potentials

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If the training of the MLP for a system does not work, there is a physical reason ⇒ must be understood

1) Data is not accurate enough

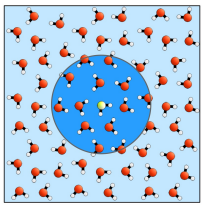
2) Descriptors are insufficient

⇒ properties of different structures are averaged ⇒ large errors

3) Physics is missing

The cutoff used in second-generation MLPs is an approximation!

⇒ Convergence tests are needed



Locality tests:

Statistical analysis:

V. L. Deringer and G. Csányi, Phys. Rev. B 95 (2017) 094203.

Hessian-based:

M. Herbold and J. Behler, J. Chem. Phys. **156** (2022) 114106.

⇒ For some systems, long-range interactions may be important!

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Third-Generation Machine Learning Potentials: Long-Range Interactions

What about electrostatics?

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Learning Electrostatic Multipoles

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Goal:

Use ML to represent flexible electrostatic charges and multipoles as a function of the molecular structure.

⇒ improved description of electrostatics in classical force fields for small molecules

Main methods: Kriging and Neural Networks

⇒ not a full MLP, since only the electrostatic component is constructed using ML

S. Houlding, S. Y. Liem and P. L. A. Popelier, Int. J. Quant. Chem. **107** (2007) 2817.

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Third-Generation Neural Network Potentials: Method

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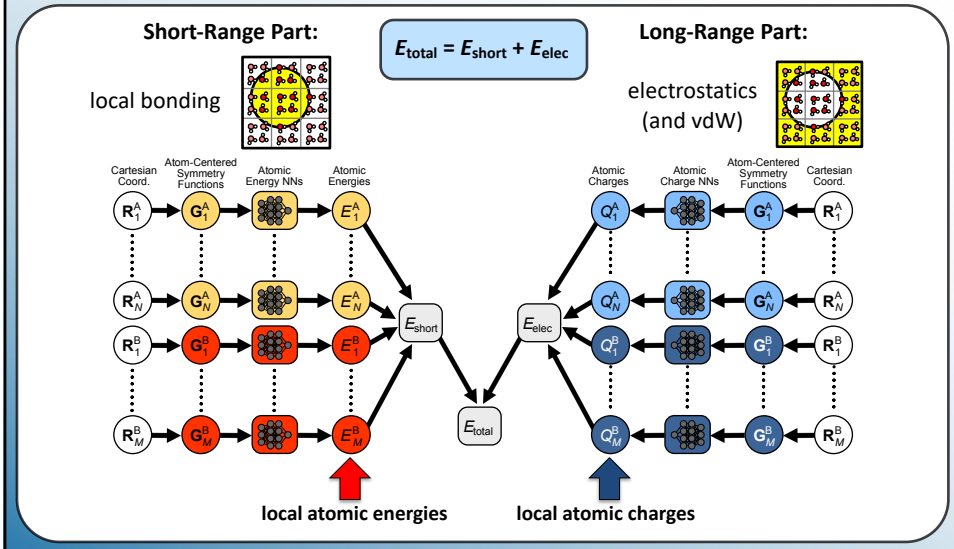

N. Artrith, T. Morawietz and J. Behler, *Phys. Rev. B* 83 (2011) 153101.
T. Morawietz and J. Behler, *J. Chem. Phys.* 136 (2012) 064103.

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Machine Learning Potentials

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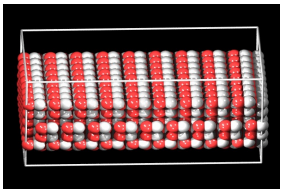
1995 2000 2005 2010 2015 2020

First-generation MLPs

Second-generation MLPs

Third-generation MLPs

Zinc Oxide Surface



Examples:

N. Artrith, T. Morawietz and J. Behler, *Phys. Rev. B* 83 (2011) 153101.
T. Morawietz and J. Behler, *J. Chem. Phys.* 136 (2012) 064103.
K Yao et al., *Chem. Sci.* 9 (2018) 2261.
O. T. Unke and M. Meuwly, *J. Chem. Theory Comput.* 15 (2019) 3678.

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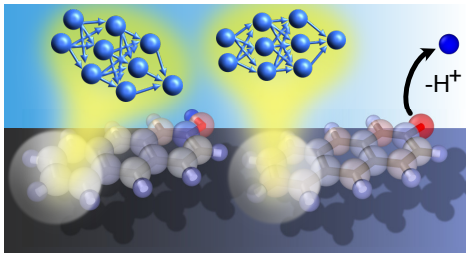
Fourth-Generation Machine Learning Potentials: Global Charge Distribution



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Limitations of Local Machine Learning Potentials

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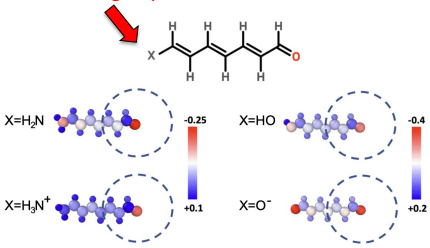
Effect of distance structural changes in molecular systems:

Example 1: C_7H_7OX

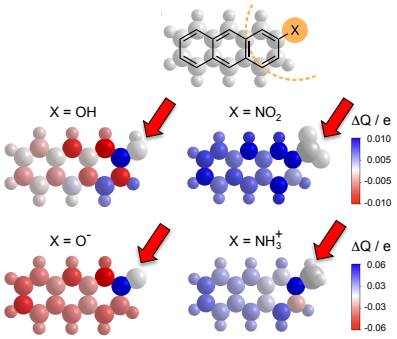
functional group



DFT Hirshfeld charges

⇒ different local properties for the same local geometry
⇒ contradictory training data

Example 2: anthracene



⇒ charge transfer determines reactivity (e.g. mesomeric effect)

T. W. Ko, J. A. Finkler, S. Goedecker, J. Behler, Nature Commun. 12 (2021) 398.

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CENT – Charge Equilibration Neural Network Technique

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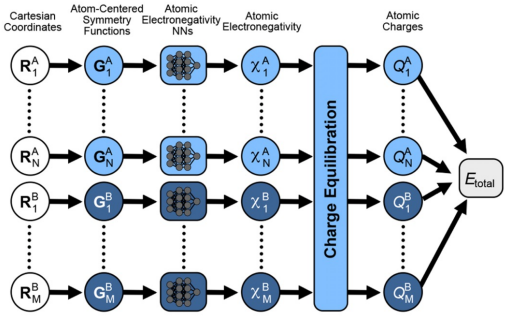
$$E_{\mathrm{tot}}(\{Q_i\}) = \sum_{i=1}^{N_{\mathrm{atom}}} \left(E_i^0 + \chi_i Q_i + \frac{1}{2} J_{ii} Q_i^2 \right) + \frac{1}{2} \iint \frac{\rho(\mathbf{R})\,\rho(\mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|} \mathrm{d}\mathbf{R}\,\mathrm{d}\mathbf{R}'$$

electronegativities — hardness — Coulomb energy



⇒ global electronic structure included (non-local charge transfer)

⇒ applications: systems with primarily ionic bonding

S. A. Ghasemi, A. Hofstetter, S. Saha, S. Goedecker, Phys. Rev. B **92** (2015) 045131.

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Fourth-Generation Neural Network Potentials: Method

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Goal: Combination of the advantages of CENT and HDNNPs

CENT

global charge distribution
⇒ electrostatics

2G-HDNNP

atomic energies
⇒ local bonding

modified training: atomic charge

additional atomic descriptor: atomic charge

4G-HDNNP

$E_{\mathrm{total}} = E_{\mathrm{short}} + E_{\mathrm{elec}}$

atomic energies + global charges
⇒ local bonding + electrostatics

T. W. Ko, J. A. Finkler, S. Goedecker, J. Behler, Nature Commun. 12 (2021) 398.
T. W. Ko, J. A. Finkler, S. Goedecker, J. Behler, Acc. Chem. Res. 54 (2021) 808.

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Fourth-Generation Neural Network Potentials: Method

RUB

Goal: Combination of the advantages of CENT and HDNNPs

glob
⇒ e

criptor:

Advantages:

- applicable to all types of bonding and systems (ionic, covalent, metallic, ...)
- long-range electrostatic interactions (flexible charges)
- description of non-local charge transfer
- applicable to multiple global charge states

atomic energies + global charges
⇒ local bonding + electrostatics

T. W. Ko, J. A. Finkler, S. Goedecker, J. Behler, Nature Commun. 12 (2021) 398.
T. W. Ko, J. A. Finkler, S. Goedecker, J. Behler, Acc. Chem. Res. 54 (2021) 808.

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Fourth-Generation Neural Network Potentials: Method

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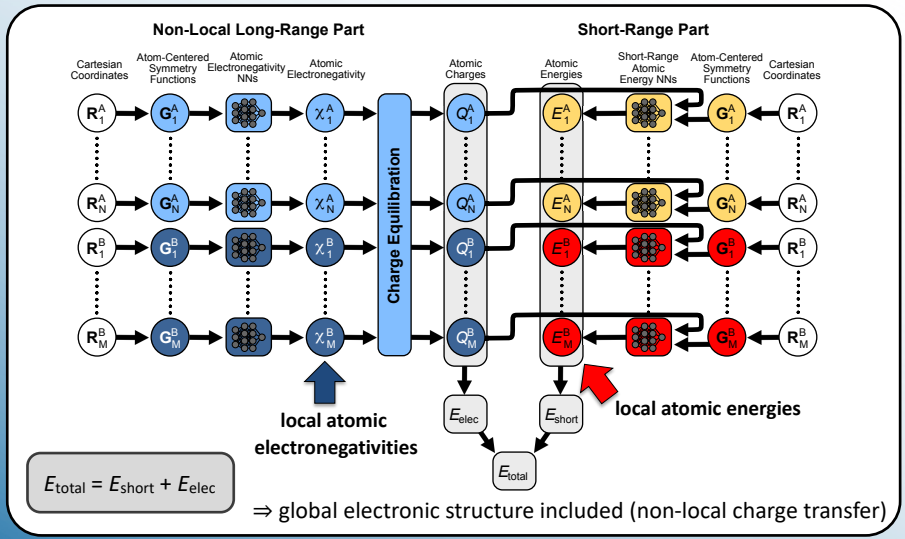

⇒ global electronic structure included (non-local charge transfer)

T. W. Ko, J. A. Finkler, S. Goedecker, J. Behler, Nature Commun. 12 (2021) 398.
T. W. Ko, J. A. Finkler, S. Goedecker, J. Behler, Acc. Chem. Res. 54 (2021) 808.

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Fourth-Generation Neural Network Potentials: Examples

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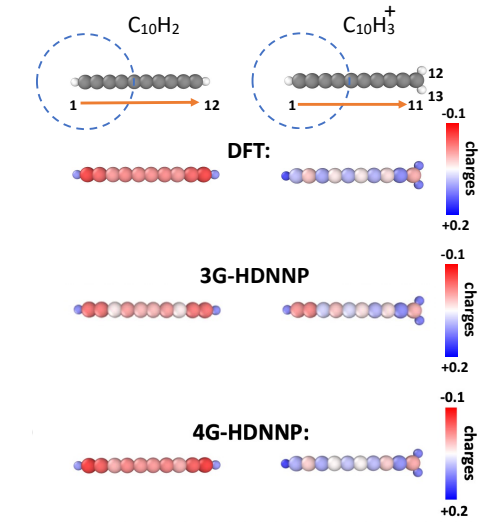
Test Case: Organic Molecules



Root Mean Squared Errors

Method		*Q* (e)	*E* (meV/ atom)	*F* (eV/Å)
2G	train	---	1.6	0.131
	test	---	1.6	0.130
3G	train	0.027	3.2	0.653
	test	0.027	3.2	0.658
4G	train	0.006	1.1	0.078
	test	0.007	1.2	0.078

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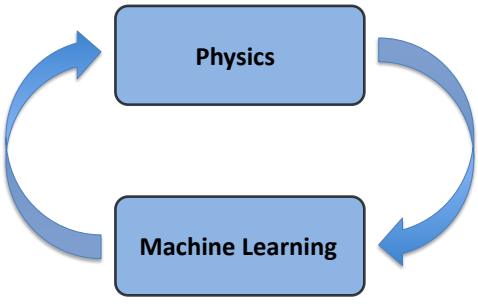
Machine Learning Potentials: Where are we now?



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Challenge: How to measure the accuracy?

To date strong focus on *E* and *F* RMSEs: "the lower the better..."

But we need to know:

- accuracy for unknown (relevant) structures
- stability in simulations
- are the trajectories correct

We need to check the right properties

⇒ a lot of effort, requires physical knowledge about the system

What is our benchmark? What is the truth?

- Theory? Experiment?

Coupled cluster calculations for large systems are impossible!
⇒ Often we do not know the truth

Good news: In DFT we have accepted this dilemma and it works!

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What to do?

- **The MLP must have a low RMSE for *E* and *F***

  Mandatory but not a sufficient criterion
  ⇒ large remaining errors indicate problems (data, descriptor, physics...)

- **Molecular dynamics must be long-term stable**

  But: long-term stability is no proof for the right physics (*"Seeing is believing"?*)
  "Well, you can run it..."

- **Understand the physics of the system before training a potential**

  ⇒ check the critical properties

  Comparison to experiment is often difficult

Validation of MLPs is become a main task

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Example:
Multiple Charge States

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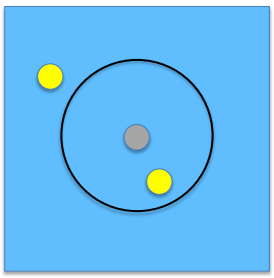
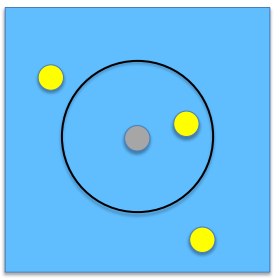
The Fe^{2+}/Fe^{3+} redox system in water

RUB

$FeCl_2$ in water



$FeCl_3$ in water



Expectation:

- A local second-generation MLP must fail for this combined system
- A global fourth-generation MLP should work for this system

How can we investigate/validate this?

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The Fe^{2+}/Fe^{3+} redox system in water

RUB

Construction of 6 HDNNPs

HDNNP	Dataset	*E* RMSE (meV/atom)	*F* RMSE (eV/Å)	*Q* RMSE (me)
2G(Fe^{2+})	$FeCl_2$/water	0.203 (0.213)	0.032 (0.032)	---
2G(Fe^{3+})	$FeCl_3$/water	0.232 (0.245)	0.037 (0.037)	---
2G(Fe^{2}+/Fe^{3+})	all	0.262 (0.271)	0.034 (0.035)	---
4G(Fe^{2+})	$FeCl_2$/water	0.203 (0.258)	0.031(0.036)	2.896 (2.896)
4G(Fe^{3+})	$FeCl_3$/water	0.237 (0.258)	0.036 (0.036)	3.130 (3.124)
4G(Fe^{2+}/Fe^{3+})	all	0.258 (0.273)	0.033 (0.033)	3.105 (3.108)

⇒ no significant difference, all very accurate (?)

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The Fe^{2+}/Fe^{3+} redox system in water

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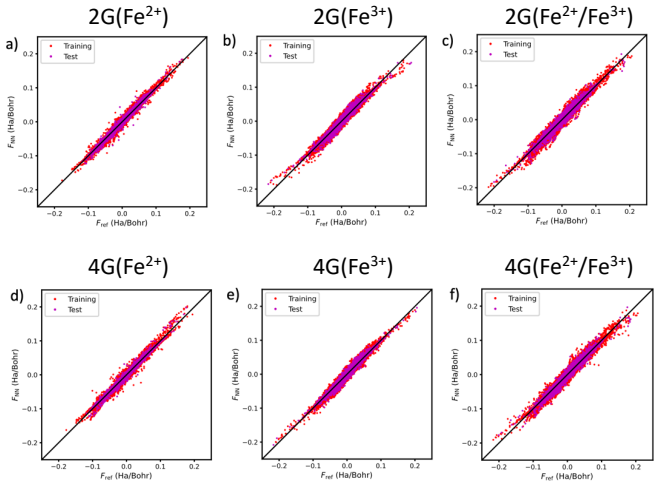
What about outliers? Force correlation plots



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The Fe^{2+}/Fe^{3+} redox system in water

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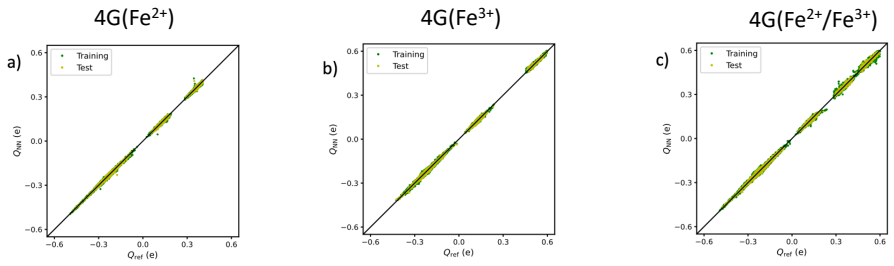
4G-HDNNP Charge Correlation



⇒ Charges of both oxidation states are well represented

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The Fe^{2+}/Fe^{3+} redox system in water

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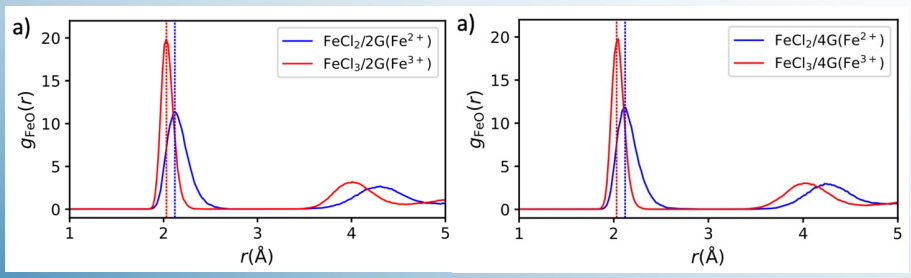
Fe-O Radial Distribution Functions:

Test 1: HDNNPs trained only to $FeCl_2$ *OR* $FeCl_3$ (15 Å box)

2G-HDNNP **4G-HDNNP**



⇒ All trajectories are stable

⇒ For separate datasets all HDNNPs work fine

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The Fe^{2+}/Fe^{3+} redox system in water

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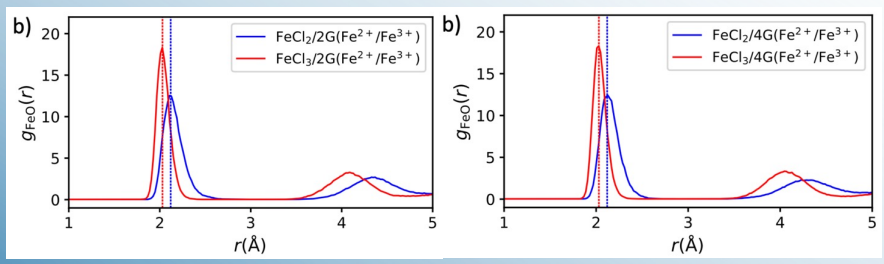
Fe-O Radial Distribution Functions:

Test 2: HDNNPs trained to $FeCl_2$ *AND* $FeCl_3$ (15 Å box)

2G-HDNNP **4G-HDNNP**



⇒ All trajectories are stable
⇒ For combined datasets all HDNNPs *SEEM* to work fine

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The Fe^{2+}/Fe^{3+} redox system in water

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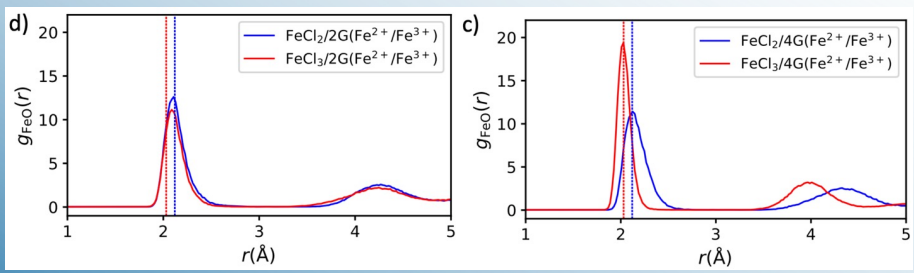
Fe-O Radial Distribution Functions:

Test 3: HDNNPs trained to $FeCl_2$ *AND* $FeCl_3$ (30 Å box)

2G-HDNNP **4G-HDNNP**



⇒ 2G-HDNNPs fail, 4G-HDNNPs are correct

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The Fe^{2+}/Fe^{3+} redox system in water

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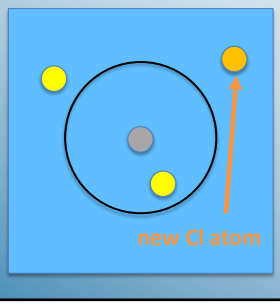
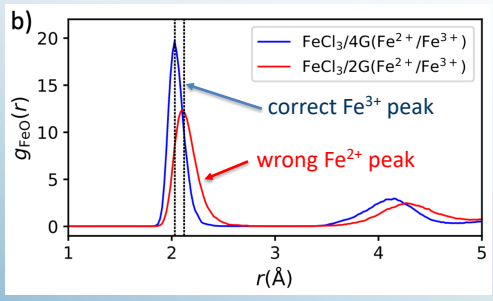
Fe-O Radial Distribution Functions:

Test 4: HDNNPs trained to $FeCl_2$ *AND* $FeCl_3$ – Addition of Cl atom

Initial structure:
$FeCl_2$ in water



Newly equilibrated system:



⇒ 2G-HDNNPs fail, 4G-HDNNPs are correct

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The Fe^{2+}/Fe^{3+} redox system in water

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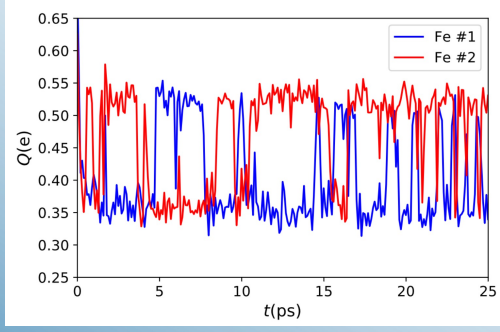
Extrapolation Test: Electron Transfer Reaction

Test: Fe_2Cl_5 in a large box of water



⇒ 4G-HDNNP can predict electron transfer and charge conservation

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Conclusions

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Conclusions

RUB

Physics remains important	⇒	Right model for the system
Real applications are important	⇒	We must go beyond model toy systems
ML not good for extrapolation	⇒	Range of validity is essential information
Reference methods are important	⇒	MLP error is smaller than DFT error
Reporting RMSEs is not enough	⇒	Stability in simulations is essential

⇒ Using Machine Learning Potentials requires physical understanding and validation

⇒ There is still a lot of room for further methodical developments

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