Atomistic Simulations with High-Dimensional Neural Network Potentials

Jörg Behler

Lehrstuhl für Theoretische Chemie II
Ruhr-Universität Bochum, Germany
and
Research Center
Chemical Sciences and Sustainability
Research Alliance Ruhr

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Overview

Topic of this talk

Machine Learning as a tool to extend the time and length scales of ab initio molecular dynamics

Goal 1: General method for all types of systems

Goal 2: Quality of reference method (here DFT)

Goal 3: Answer questions that cannot be answered with AIMD directly

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Introduction

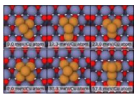
RUB

Goal:

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

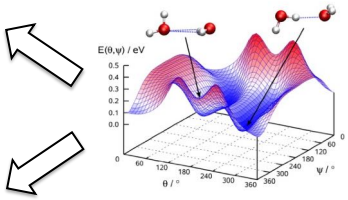
⇒ Predictive computer simulations with first-principles quality

Energy
global and local minima

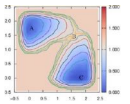


Forces
dynamics, free energies

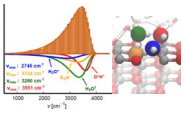
Central Role:
Potential Energy Surface



Reactions
barriers / transition states



Vibrations
properties, analysis



The accuracy of the obtained results depends on the quality of the atomic interaction

3

Potentials for Different Length and Time Scales

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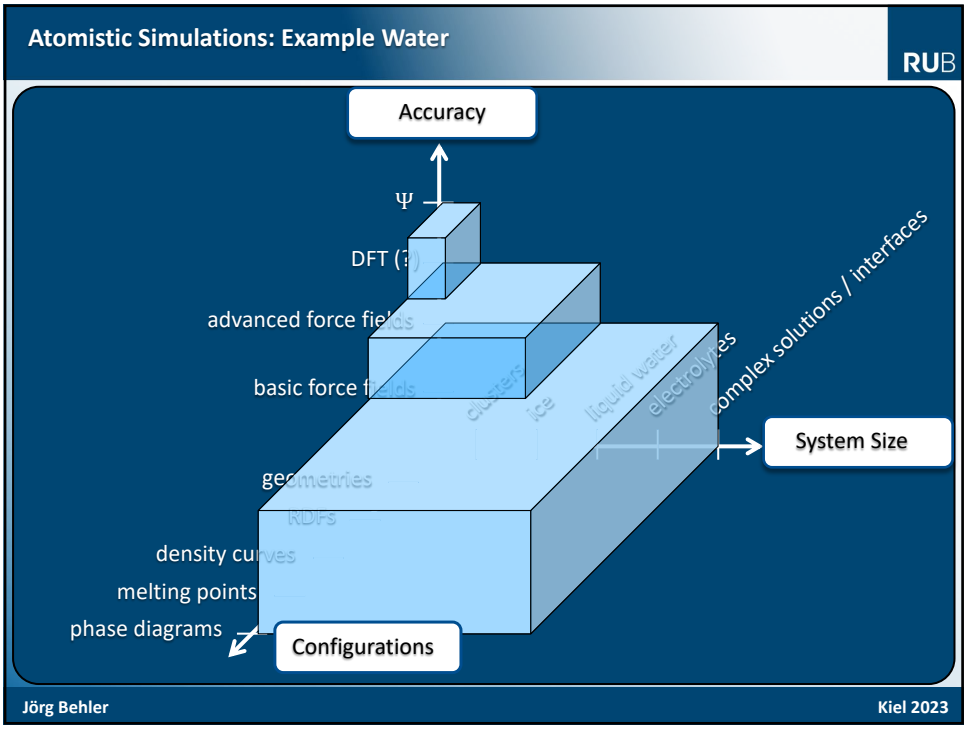
⇒ PES is the central quantity for atomistic simulations

Method	Atoms	Simulation Time
CI, CC, MP2, MP4, …	10 - 100	0
Density Functional Theory	100 - 1000	100 ps
Semiempirical Methods Tight Binding	1000 - 10 000	1 ns
„Reactive Potentials“ EAM, Tersoff, …	1000 - 100 000	10 ns
Classical Force Fields (LJ, harmonic, Coulomb)	1 000 000	1 ms

4


Atomistic Simulations: Example Water
RUB
Accuracy
Ψ
DFT (
advanced force fields
basic force fields
clusters
ice
liquid water
electrolytes
complex solutions / interfaces
System Size
geometries
RDFs
density curves
melting points
phase diagrams
Configurations
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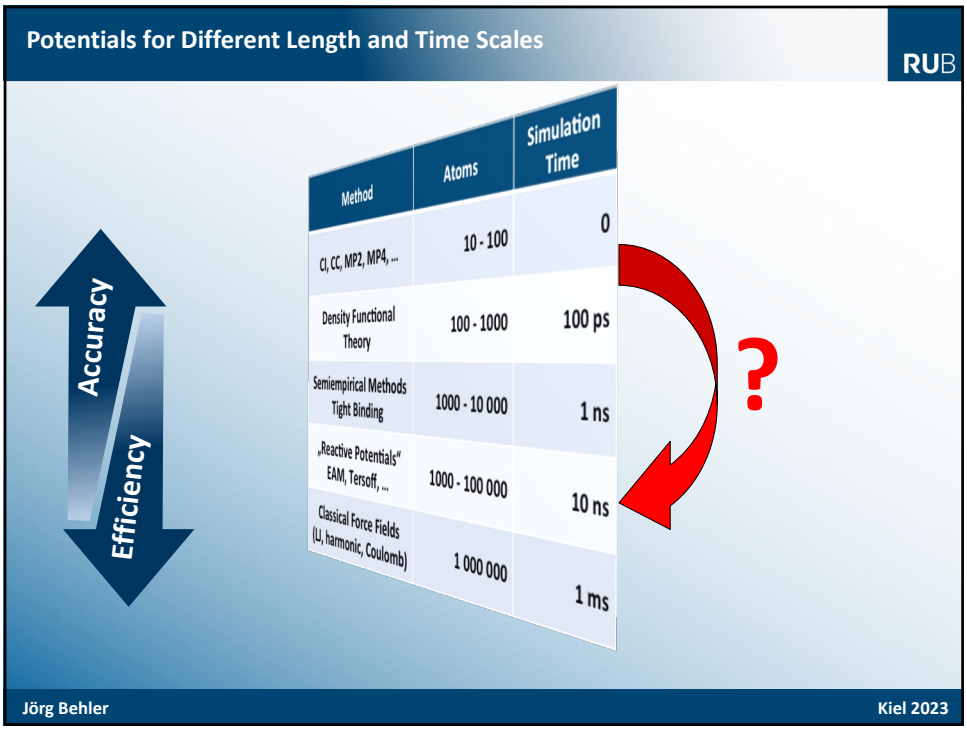
Potentials for Different Length and Time Scales
RUB
Accuracy
Efficiency
Method
Atoms
Simulation Time
CI, CC, MP2, MP4, ...
10 - 100
0
Density Functional Theory
100 - 1000
100 ps
Semiempirical Methods Tight Binding
1000 - 10 000
1 ns
„Reactive Potentials" EAM, Tersoff, ...
1000 - 100 000
10 ns
Classical Force Fields (U, harmonic, Coulomb)
1 000 000
1 ms
?
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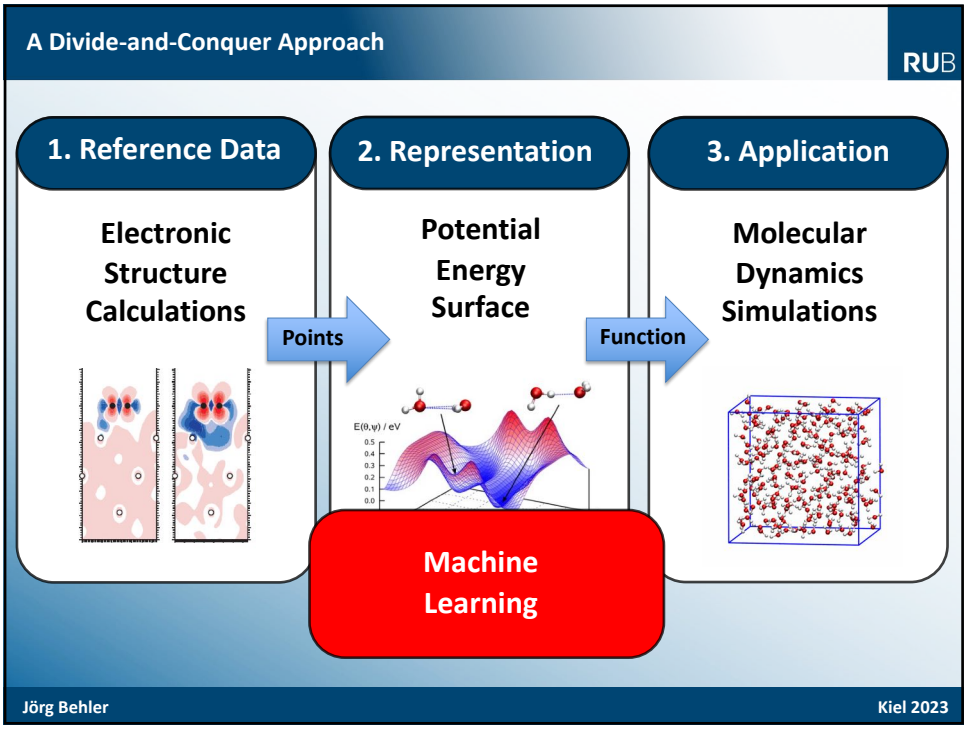
A Divide-and-Conquer Approach
RUB
1. Reference Data
2. Representation
3. Application
Electronic Structure Calculations
Points
Potential Energy Surface
Function
Molecular Dynamics Simulations
Machine Learning
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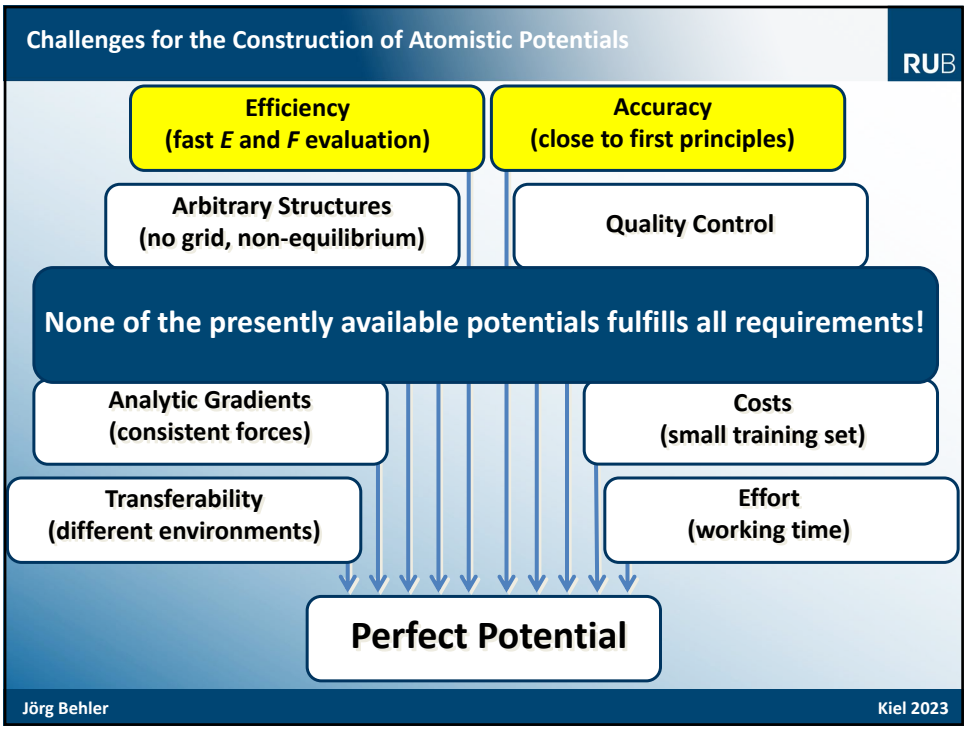
Challenges for the Construction of Atomistic Potentials
RUB
Efficiency (fast E and F evaluation)
Accuracy (close to first principles)
Arbitrary Structures (no grid, non-equilibrium)
Quality Control
None of the presently available potentials fulfills all requirements!
Analytic Gradients (consistent forces)
Costs (small training set)
Transferability (different environments)
Effort (working time)
Perfect Potential
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Neural Network Potentials

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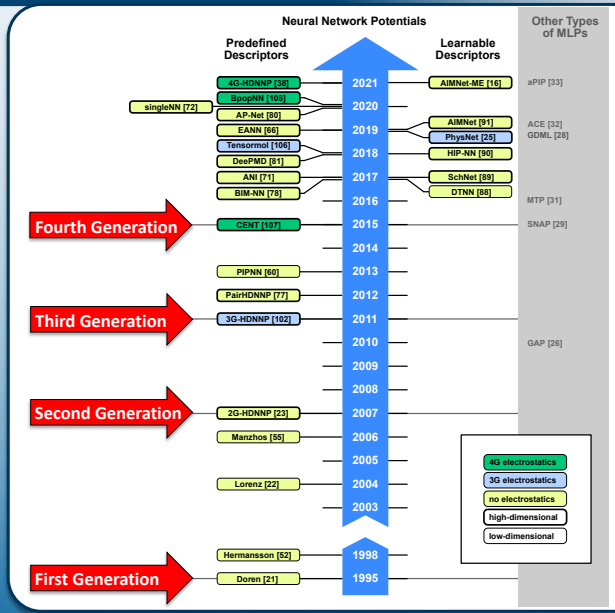

J. Behler, *Chem. Rev.* 121 (2021) 10037.

E. Kocer, T. W. Ko, J. Behler, *Ann. Rev. Phys. Chem.*, in press (2022).

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First-Generation Neural Network Potentials 1995 – 2007

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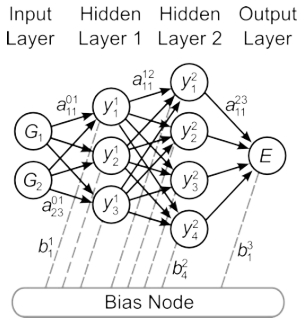
Machine Learning Potentials

RUB

1995 2000 2005 2010 2015 2020

First Machine Learning Potential = First Neural Network Potential

T.B. Blank, S.D. Brown, A.W. Calhoun, and D.J. Doren, *J. Chem. Phys.* **103** (1995) 4129.



Feed-forward neural network

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Machine Learning Potentials

RUB

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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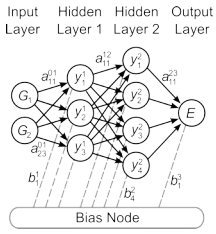
Machine Learning Potentials

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)

⇒ No generally applicable solution for all systems

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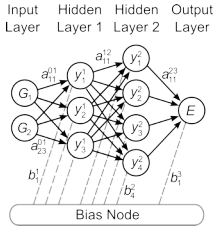
Machine Learning Potentials

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

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Second-Generation Neural Network Potentials: Locality

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High-Dimensional Neural Network Potentials

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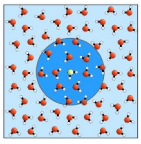
3 Steps:

1. Total energy is the sum of atomic energies

$$E = \sum_i E_i$$

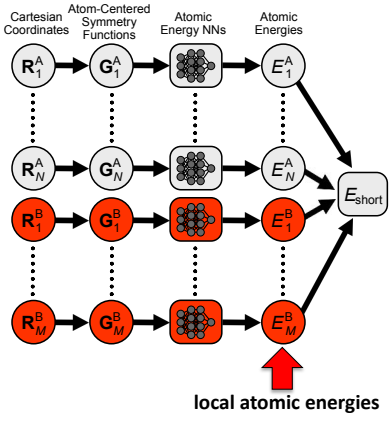
2. Atomic energies depend on local environments
   ⇒ cutoff radius



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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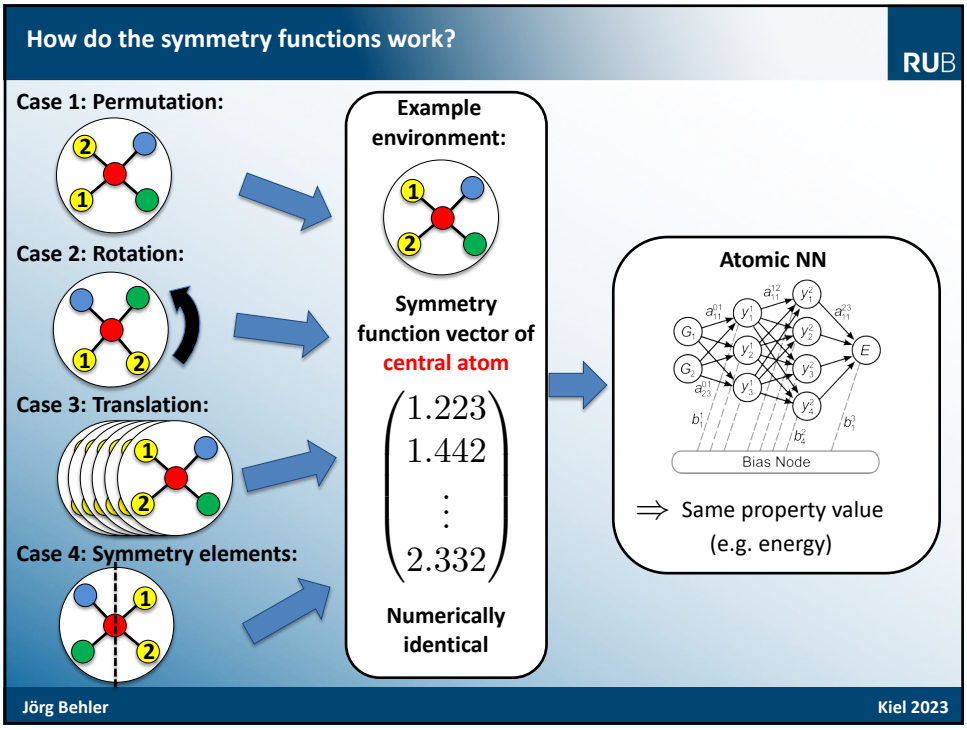
How do the symmetry functions work?
RUB
Case 1: Permutation:
Case 2: Rotation:
Case 3: Translation:
Case 4: Symmetry elements:
Example environment:
Symmetry function vector of central atom
1.223
1.442
2.332
Numerically identical
Atomic NN
Bias Node
⇒ Same property value (e.g. energy)
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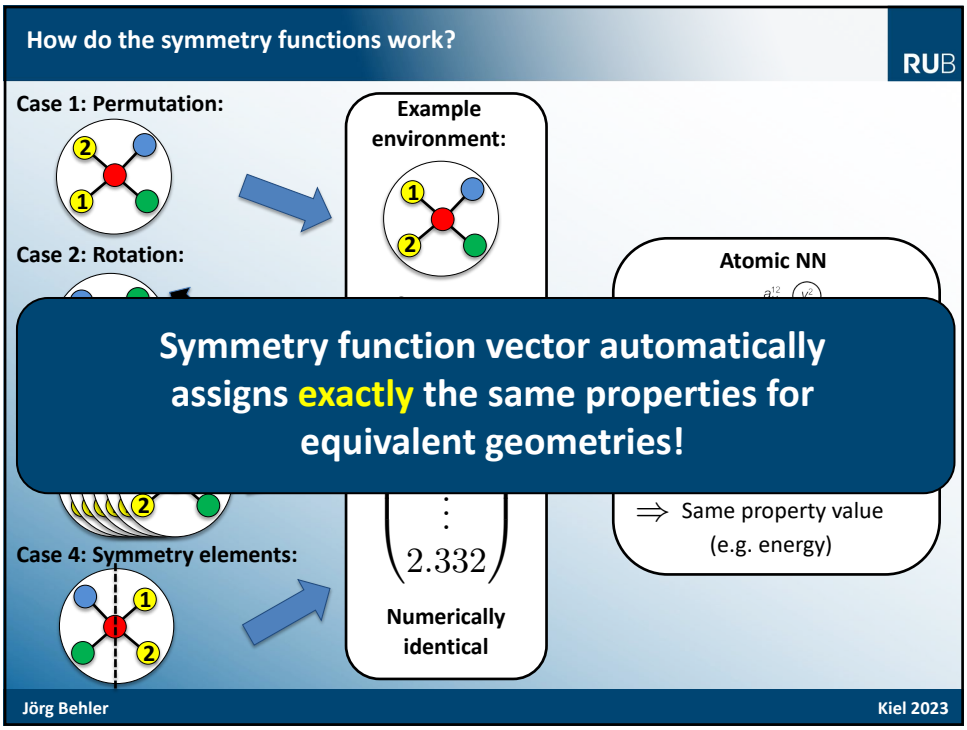
How do the symmetry functions work?
RUB
Case 1: Permutation:
Case 2: Rotation:
Case 4: Symmetry elements:
Example environment:
Atomic NN
Symmetry function vector automatically assigns exactly the same properties for equivalent geometries!
2.332
Numerically identical
⇒ Same property value (e.g. energy)
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Symmetry Functions: Cutoff Function

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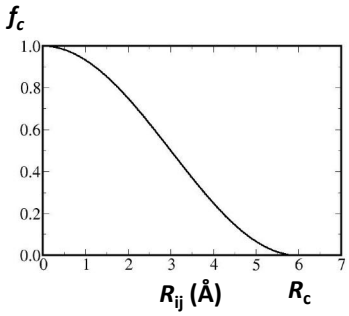
Cutoff Function

- decays to zero in value and slope at R_c
- reflects decreasing chemical interaction
- central component of all symmetry functions
- R_c is increased until potential converges

$$f_c(R_{ij}) = \begin{cases} \frac{1}{2}\left[\cos\left(\frac{\pi R_{ij}}{R_c}\right)+1\right] & \text{for} \quad R_{ij} < R_c \\ 0 & \text{for} \quad R_{ij} > R_c \end{cases}$$



Typical cutoff radius: R_c = 6 - 8 Å

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Symmetry Functions: Radial Functions

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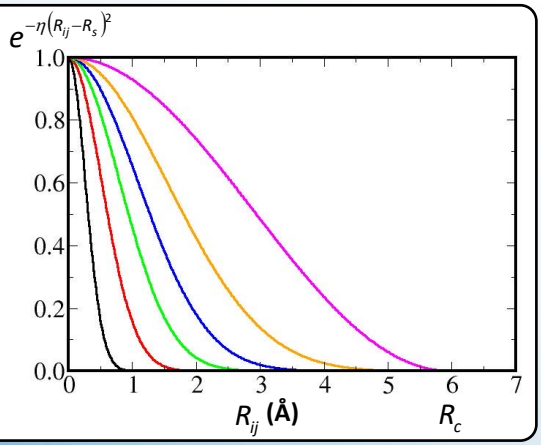
- decay with increasing distance ⇒ Gaussians
- summation over all neighbors
- many-body term, interpretation as coordination number
- one-to-one correspondence between function value and R_{ij}

$$G_i^{rad} = \sum_j e^{-\eta(R_{ij}-R_s)^2} f_c(R_{ij})$$

Set of radial functions:
„Radial Fingerprint“



J. Behler, *J. Chem. Phys.* 134 (2011) 074106.

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Symmetry Functions

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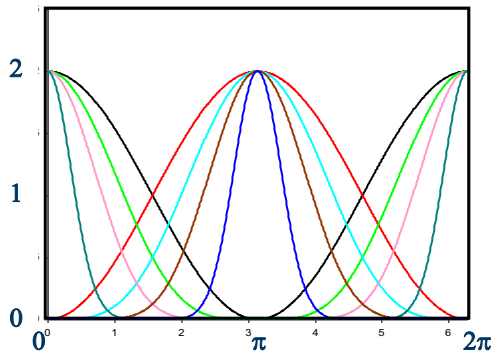
Angular symmetry functions

$$G_i^{\mu} = 2^{1-\xi} \sum_{j,k \neq i} \left(1 + \lambda \cos\theta_{ijk}\right)^{\xi} \cdot e^{-\eta\left(R_{ij}^2 + R_{ik}^2 + R_{jk}^2\right)} f_c\left(R_{ij}\right) f_c\left(R_{ik}\right) f_c\left(R_{jk}\right)$$



⇒ **Several angular functions are used**

- **all symmetry functions are many-body terms**
- **typical number: about 10 radial and 40 angular functions**

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Symmetry Functions: Combinatorial Growth

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For an *N* element system, there are *N* separate atomic NN types
⇒ no significant increase in complexity

For each radial function there are *N* functions for the possible neighboring elements
⇒ increase in complexity

For each angular function there are *N(N+1)/2* functions for the neighboring elements
⇒ strong increase in complexity

Elements	atomic NNs	multiplier radial/angular symmetry functions	typical total number of symmetry functions
1	1	1 / 1	6 + 25
2	2	2 / 3	12 + 75
3	3	3 / 6	18 + 150
4	4	4 / 10	24 + 250

Often, a reduction is possible, if only some compositions or structures are relevant

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Construction of the Reference Set: Active Learning

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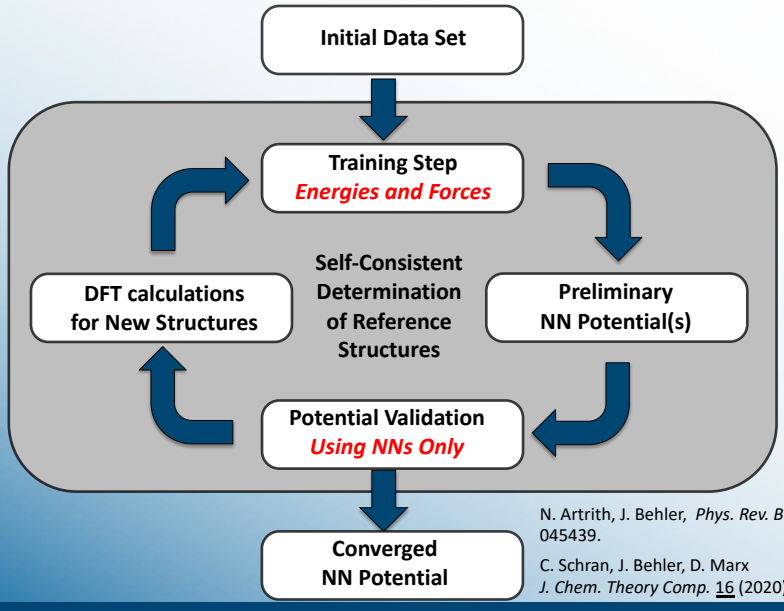

N. Artrith, J. Behler, *Phys. Rev. B.* 85 (2012) 045439.

C. Schran, J. Behler, D. Marx *J. Chem. Theory Comp.* 16 (2020) 88.

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Is it Worth the Effort?

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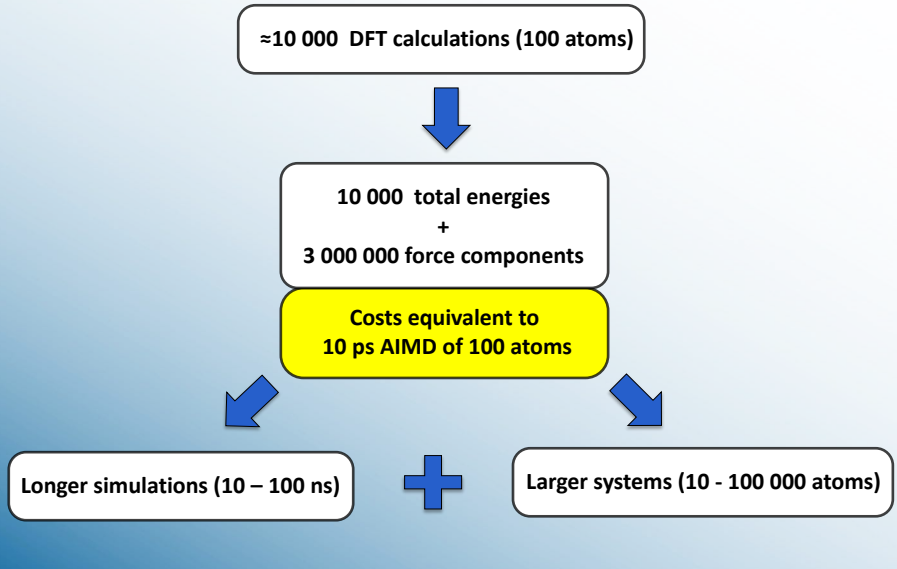

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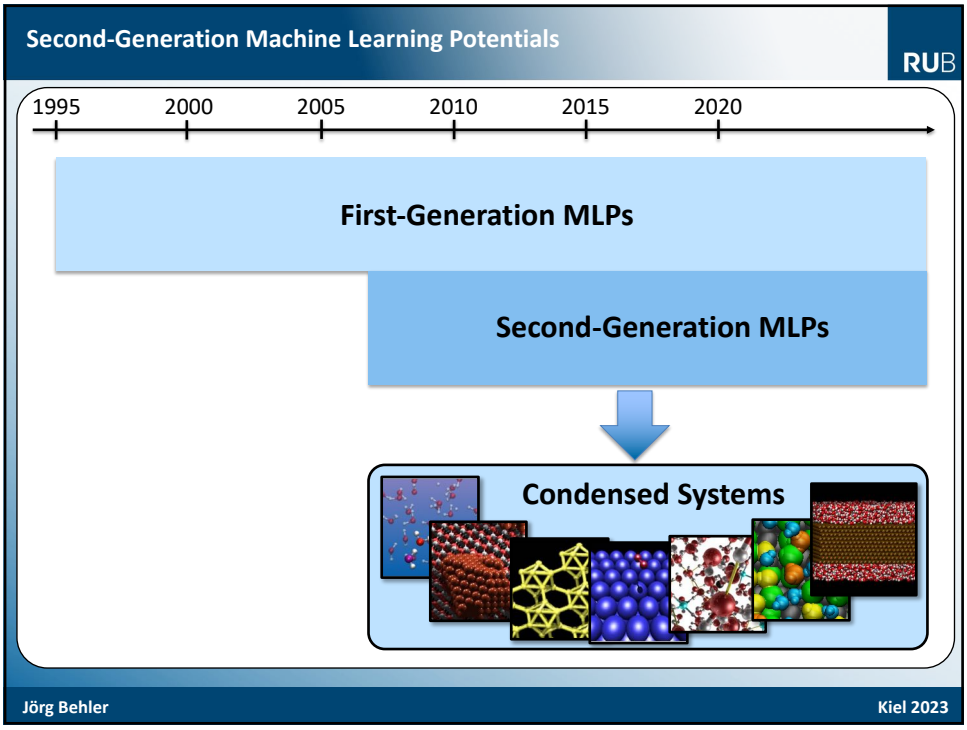
Second-Generation Machine Learning Potentials
RUB
1995
2000
2005
2010
2015
2020
First-Generation MLPs
Second-Generation MLPs
Condensed Systems
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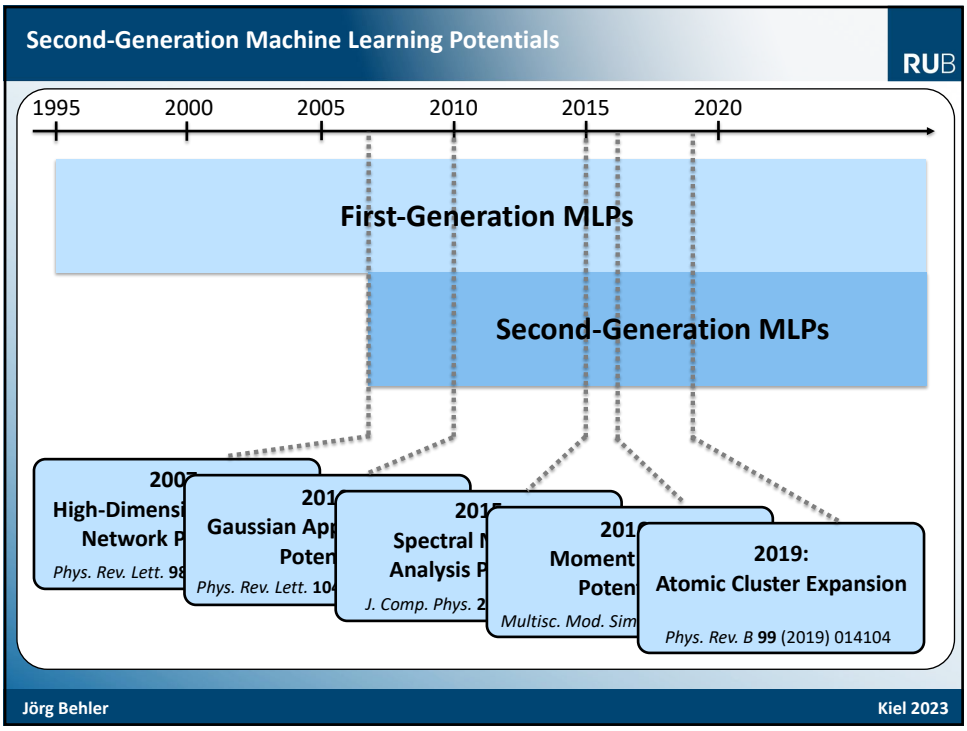
Second-Generation Machine Learning Potentials
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First-Generation MLPs
Second-Generation MLPs
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Analysis P
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2019:
Atomic Cluster Expansion
Phys. Rev. B 99 (2019) 014104
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Second-Generation Machine Learning Potentials

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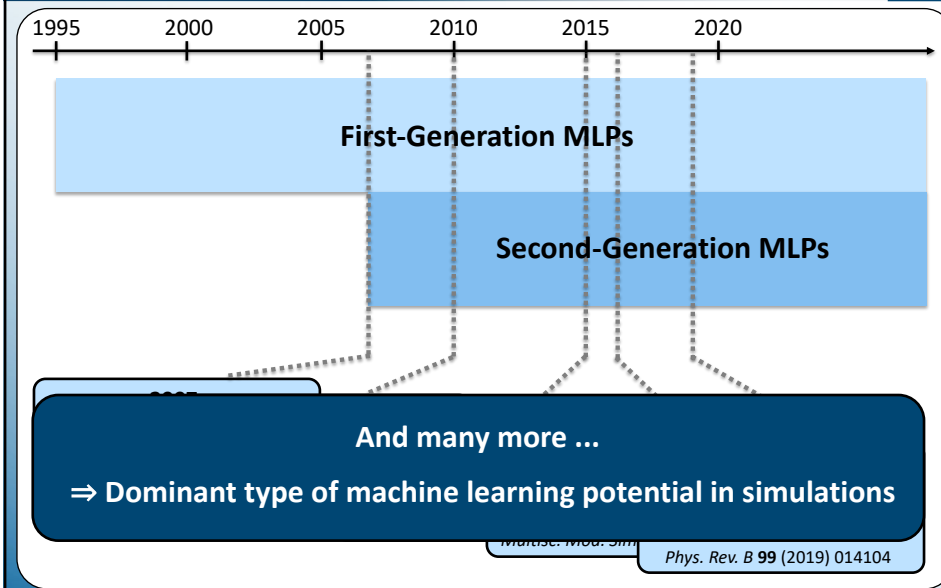

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Interaction Range

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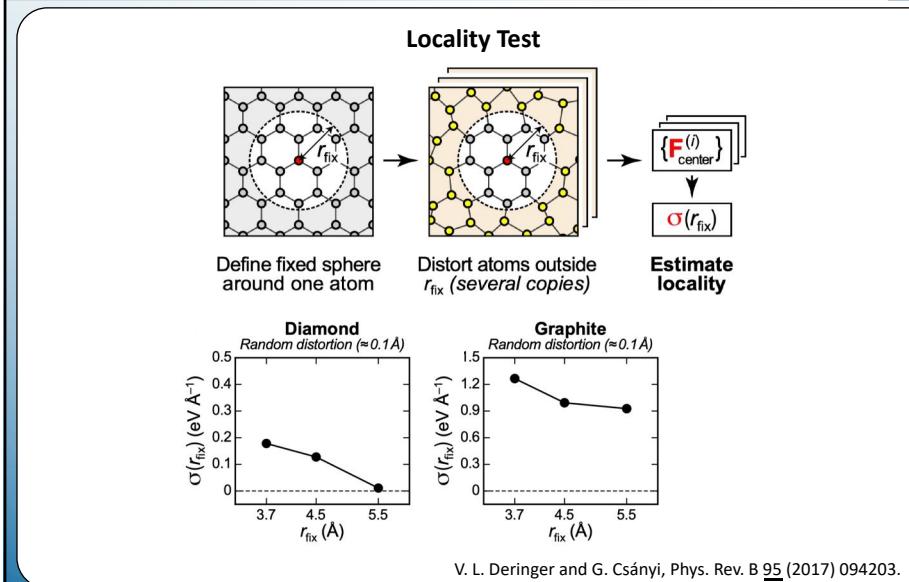

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Interaction Range

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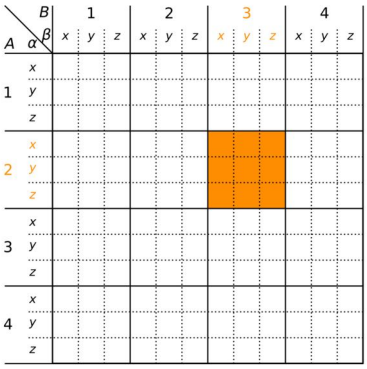
A Hessian-Based Analytic Locality Test

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



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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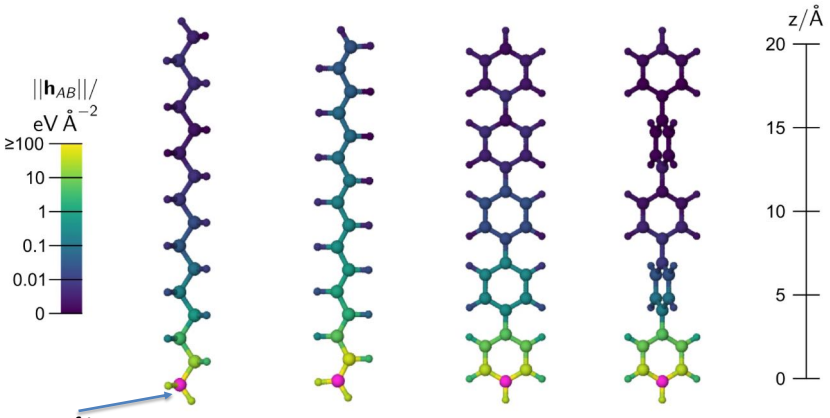
Interaction Range

RUB

A Hessian-Based Analytic Locality Test



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

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

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Third-Generation Neural Network Potentials: Long-Range Interactions

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Third-Generation Neural Network Potentials: Method

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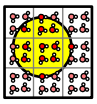
Short-Range Part:

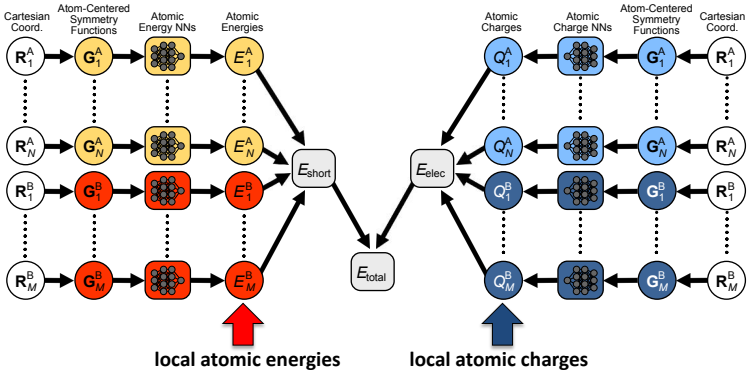
local bonding



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

Long-Range Part:

electrostatics (and vdW)



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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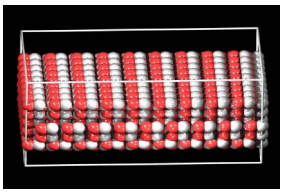
1995 2000 2005 2010 2015 2020

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 Neural Network Potentials: Global Electronic Structure

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Fourth-Generation Neural Network Potentials

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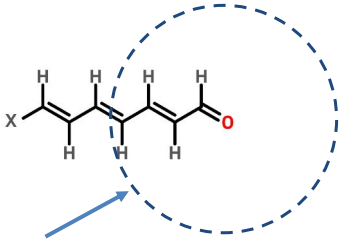
The Challenge:

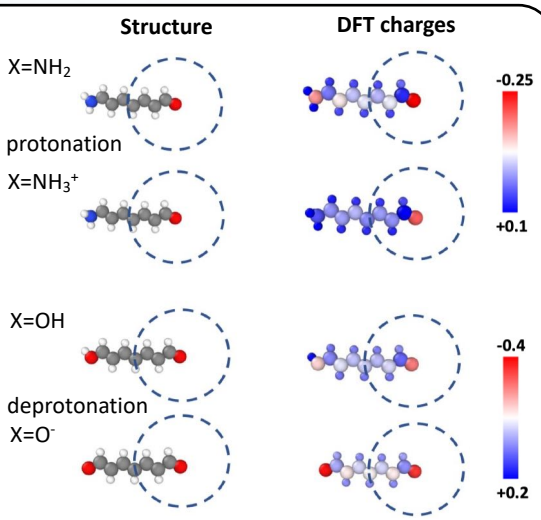
Example molecule:



cutoff radius

X = functional group

⇒ oxygen does not see the functional group X



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

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Overview: Fourth-Generation Methods

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2015: Charge Equilibration Neural Network Technique - CENT

Idea: Global charge equilibration + Charge-dependent total energy expression

Applicability: ionic inorganic systems

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

2020: Becke Population Neural Networks - BpopNN

Idea: SCF charge distribution, populations as additional inputs in modified SOAP

Applicability: molecular systems

X. Xie, K. A. Persson, D. W. Small, J. Chem. Theory Comput. 16 (2020) 4256.

2021: Fourth-Generation High-Dimensional NNPs – 4G-HDNNP

Idea: Global charge equilibration + accurate short-range energies

Applicability: very general

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

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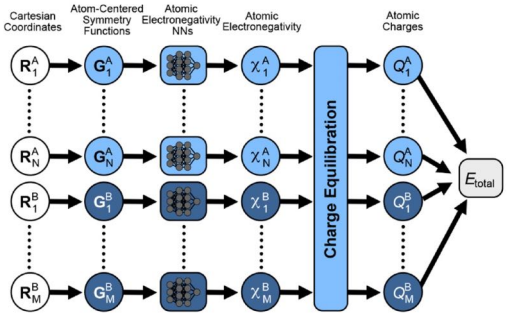
CENT – Charge Equilibration Neural Network Technique

RUB

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

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.

37

Fourth-Generation Neural Network Potentials: Method

RUB

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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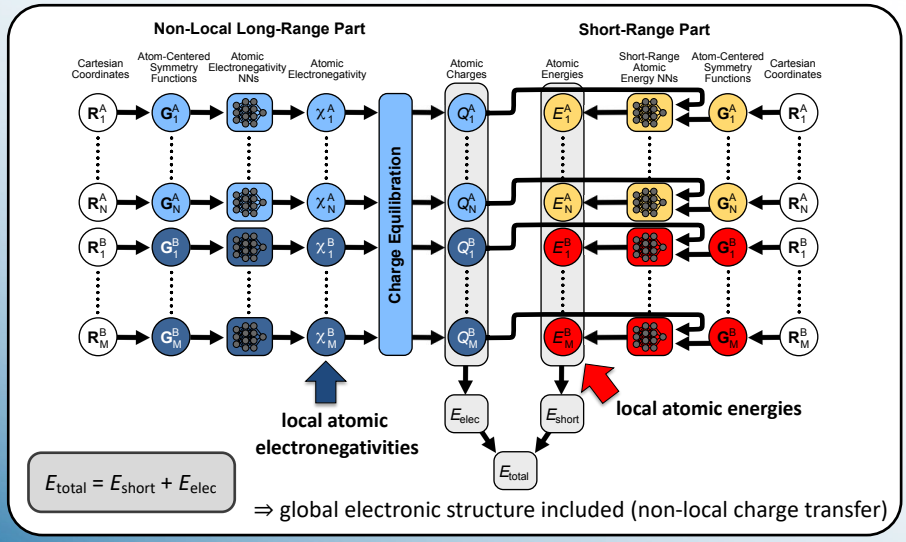
Fourth-Generation Neural Network Potentials: Method

RUB



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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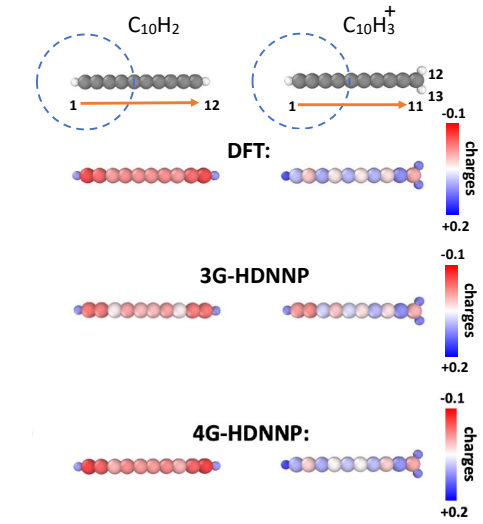
Fourth-Generation Neural Network Potentials: Examples

RUB

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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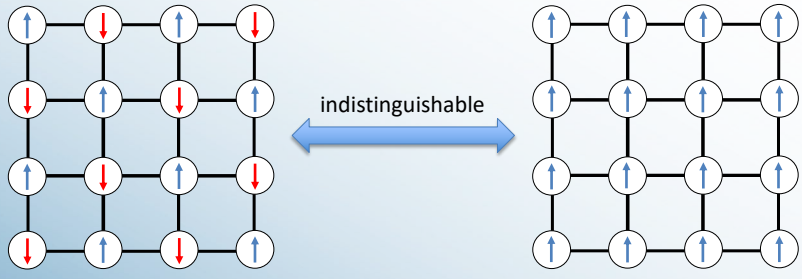
What About Magnetism?

42

Most descriptors do not depend on atomic spins



⇒ spin-related energy changes are treated as noise
⇒ unreliable energy surfaces
⇒ improved descriptors are needed

M. Eckhoff and J. Behler, *npj Comput. Mater.* **7** (2021) 170.

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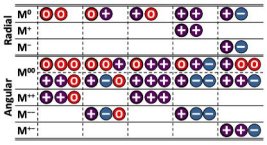
Spin-Dependent Atom-Centered Symmetry Functions (sACSF)

Step 1: Atomic spin coordinates (collinear spin)

$$s_i = \begin{cases} 0 & \text{for } |M_S| < M_S^{\text{thres}} \\ \text{sgn}(M_S) & \text{otherwise} \end{cases} \quad \text{with} \quad M_S = \tfrac{1}{2}(n_\uparrow - n_\downarrow)$$

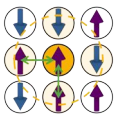
Step 2: Spin-augmentation functions (SAF), radial case

$$M^0(s_i, s_j) = 1\ ,$$
$$M^+(s_i, s_j) = \tfrac{1}{2}\,|s_i s_j| \cdot |s_i + s_j| \quad \Rightarrow \text{spin-sensitive filter}$$
$$M^-(s_i, s_j) = \tfrac{1}{2}\,|s_i s_j| \cdot |s_i - s_j|$$



Step 3: sACSF, radial case

$$G_i^{\text{rad}} = \sum_j M^x(s_i, s_j) \cdot \mathrm{e}^{-\eta R_{ij}^2} \cdot f_c\,(R_{ij})$$



⇒ Second-generation (environment-dependent) extension

⇒ Magnetic High-Dimensional Neural Network Potentials

M. Eckhoff and J. Behler, *npj Comput. Mater.* **7** (2021) 170.

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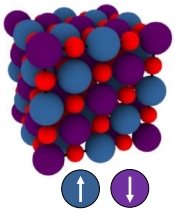
Magnetic High-Dimensional Neural Network Potentials

RUB

Application: Manganese Oxide (MnO)

- antiferromagnetic ground state (AFM-II) with rhombohedral distortion
- magnetic cell is 2x2x2 supercell of geometric unit cell



Training RMSE energy (3000 2x2x2 supercells, HSE06 functional):

HDNNP: 11 meV/atom (AFM-II = FM)

mHDNNP: 1 meV/atom (AFM II ≠ FM)

Results ΔE(AFM-II /FM) mHDNNP: 46.3 meV/atom (HSE06: 45.9 meV/atom)

Lattice parameters AFM-II
mHDNNP: a = 4.433 Å, α = 90.77°
HSE06: a = 4.434 Å, α = 90.89°
Exp.: a = 4.430 Å, α = 90.62°

M. Eckhoff and J. Behler, *npj Comput. Mater.* **7** (2021) 170.

How do we know if a Neural Network Potential is reliable?

What can we do with Neural Network Potentials?

Quality Control

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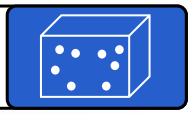
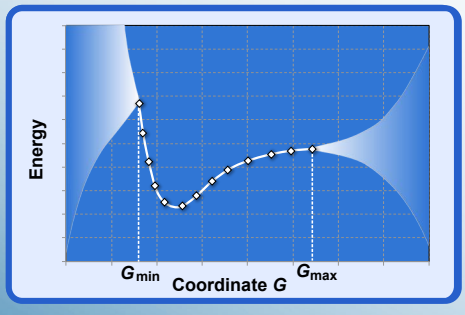
Multistep Quality Control

RUB

1. Generate reasonable initial training set
⇒ preliminary NN potential



2. Check for extrapolation



⇒ easy to detect

J. Behler, Angew. Chem. Int. Ed. 56 (2017) 12828.

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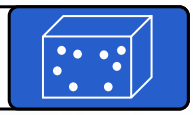
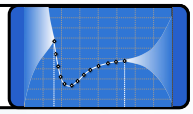
Multistep Quality Control

RUB

1. Generate reasonable initial training set
⇒ preliminary NN potential



2. Check for extrapolation
⇒ extend sampled "volume" in configuration space



3. Use a validation set ("Early Stopping Method")

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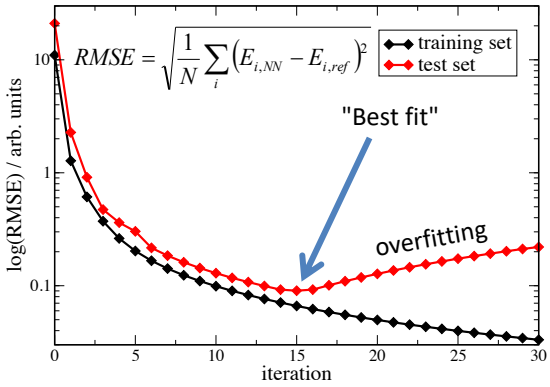
Neural Network Potentials: Early Stopping Method

RUB

Reference set → Training set: 90 %
Reference set → Test set: 10 %

Generalization → Cross Validation Methods



⇒ overfitting cannot be detected by monitoring the error of the training set

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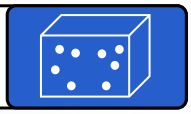
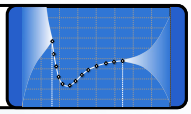
Multistep Quality Control

RUB

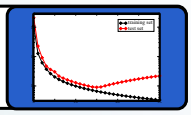
1. Generate reasonable initial training set
⇒ preliminary NN potential



2. Check for extrapolation
⇒ extend sampled "volume" in configuration space



3. Use a validation set ("Early Stopping Method")
⇒ estimate accuracy for similar structures not included in the training set



4. Check for "holes in the training set"

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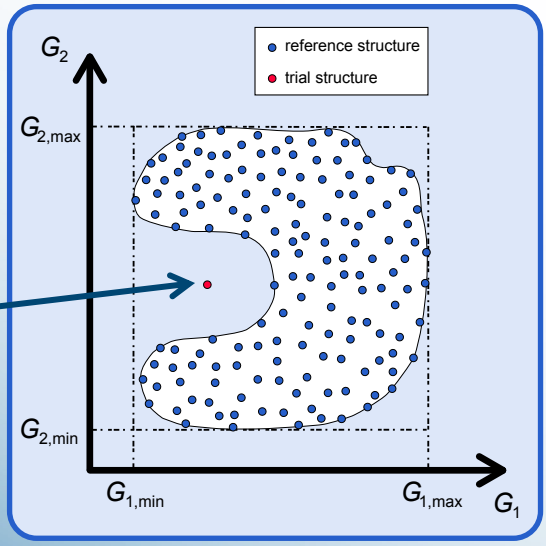
Detection of Problematic Configurations

RUB



Problem:
cannot be detected by
- extrapolation analysis
- early stopping method

⇒ Early stopping method (training and test set) is not sufficient!

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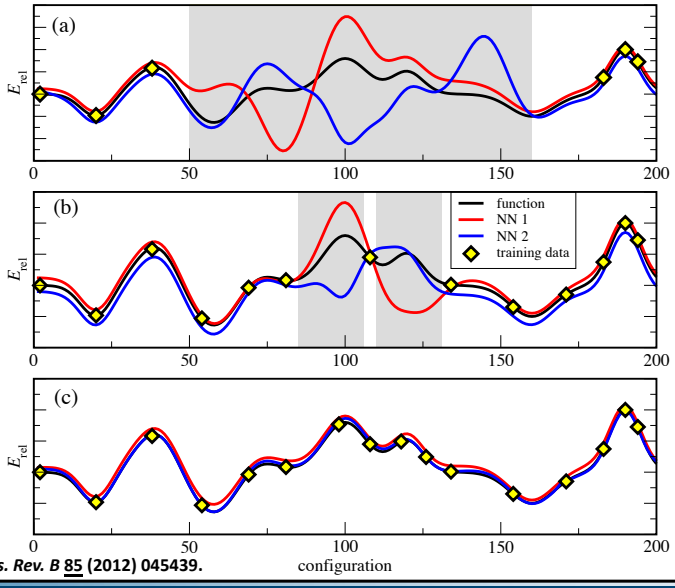
Iterative Improvement of the Reference Set

RUB

initial NN

improved NN

final NN



N. Artrith and J. Behler, *Phys. Rev. B* 85 (2012) 045439.

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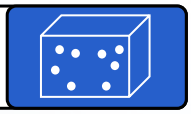
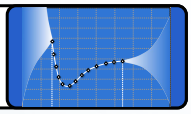
Multistep Quality Control

RUB

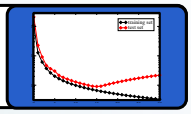
1. Generate reasonable initial training set
⇒ preliminary NN potential



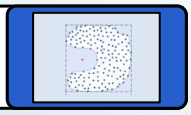
2. Check for extrapolation
⇒ extend sampled "volume" in configuration space



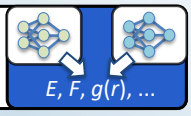
3. Use a validation set ("Early Stopping Method")
⇒ estimate accuracy for similar structures not included in the training set



4. Check for "holes in the training set"
⇒ add structures in poorly sampled regions (iteratively)



5. Check robustness of the results
⇒ repeat simulations with independent NN potentials



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Applications

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Materials Science: Crystal Structure Prediction

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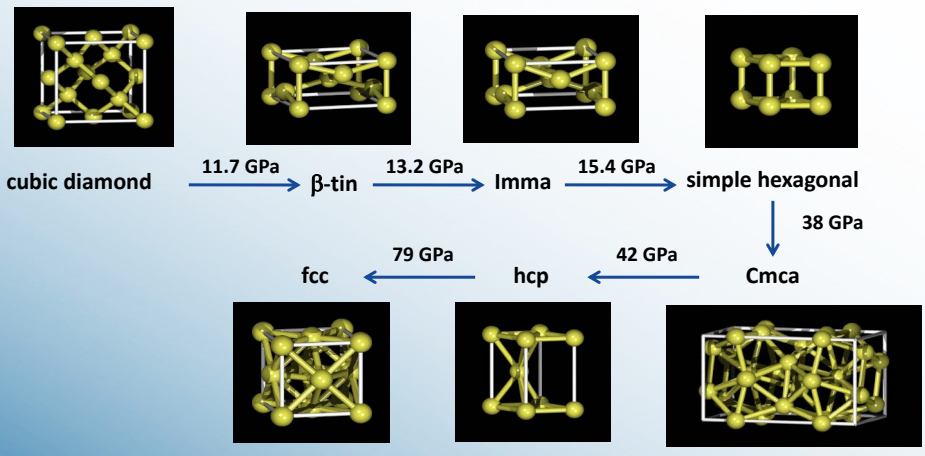
High-Pressure Phase Diagram of Silicon

RUB



Review: A. Mujica, A. Rubio, A. Muñoz, and R.J. Needs, *Rev. Mod. Phys.* 75, 863 (2003).

⇒ Challenging model system to test potentials

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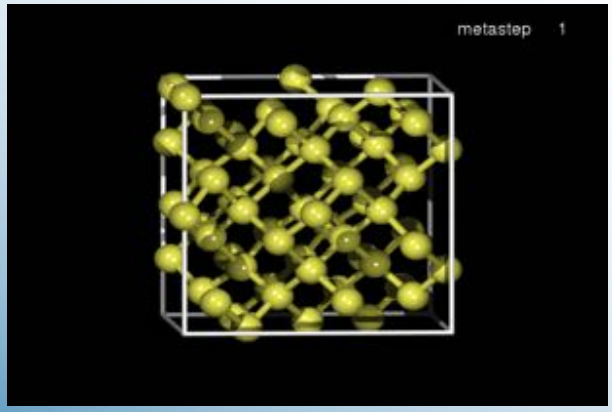
Metadynamics Simulations of Silicon

RUB

diamond → β-Sn → Imma → sh → Cmca → hcp → fcc

T = 300 K, *p* = 12 Gpa, 200 ps MD

Movie contains only the final frame of each metastep



J. Behler, M. Parrinello, *Phys. Rev. Lett.* 98 (2007) 146401.
J. Behler, R. Martoňák, D. Donadio, and M. Parrinello, *Phys. Rev. Lett.* 100 (2008) 185501.

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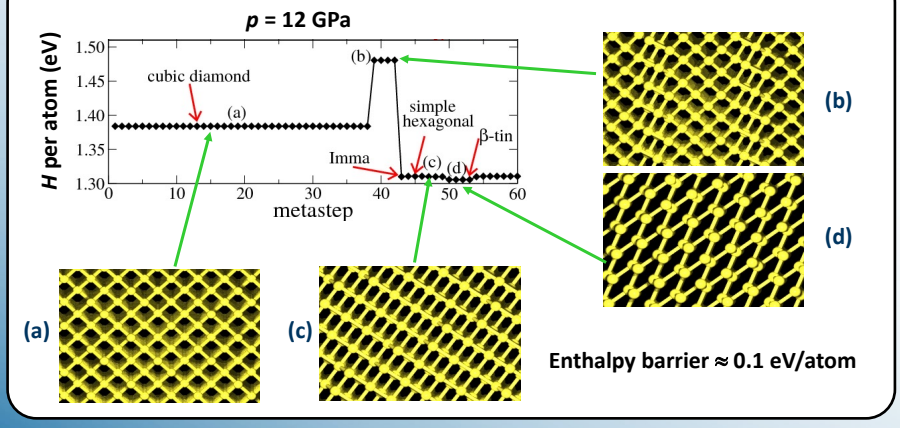
Metadynamics Simulations of Silicon

RUB

diamond → β-Sn → Imma → sh → Cmca → hcp → fcc



J. Behler, M. Parrinello, *Phys. Rev. Lett.* 98 (2007) 146401.
J. Behler, R. Martoňák, D. Donadio, and M. Parrinello, *Phys. Rev. Lett.* 100 (2008) 185501.

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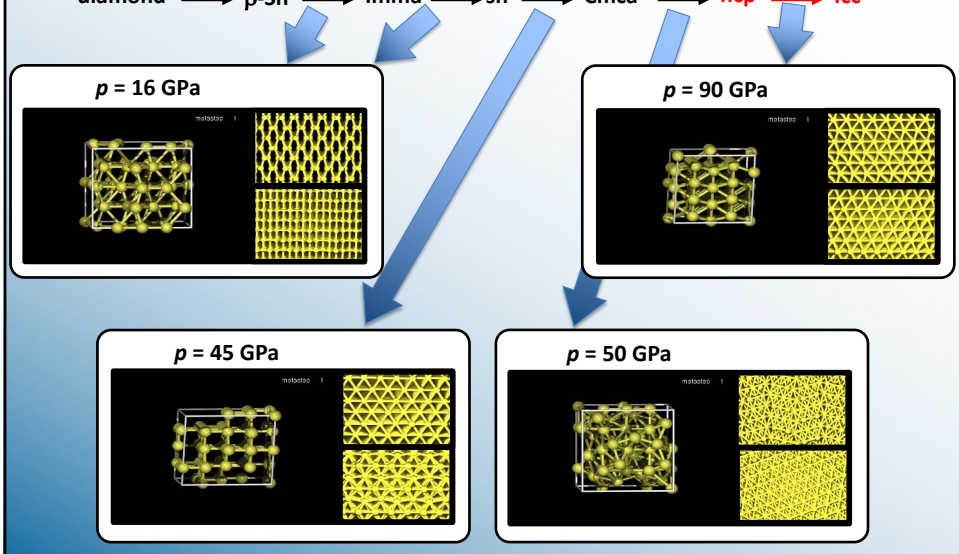
A "Walk" through the High Pressure Phase Diagram of Silicon

RUB

diamond → β-Sn → Imma → sh → Cmca → hcp → fcc



60

Prediction of the High-Pressure Phase Diagram of Silicon

RUB

⇒ NN-based simulations have DFT quality
(and excellent agreement with experiment)

⇒ Predictive simulations impossibe with DFT (costs!)
or other potentials like EAM, tight binding, … (too low accuracy)

Simulation Costs

≈ 100 simulations x 100 metasteps x 2 ps MD (stress tensor)
⇒ 20 000 000 energy and force evaluations

DFT:
⇒ ≈ 20 000 CPU *years* per phase diagram (8 M€ hardware "consumption")

NN:
⇒ ≈ 20 CPU *years* per phase diagram (8 k€ hardware "consumption")

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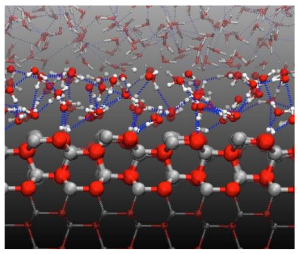
Solid-Liquid Interfaces: Water-Zinc Oxide



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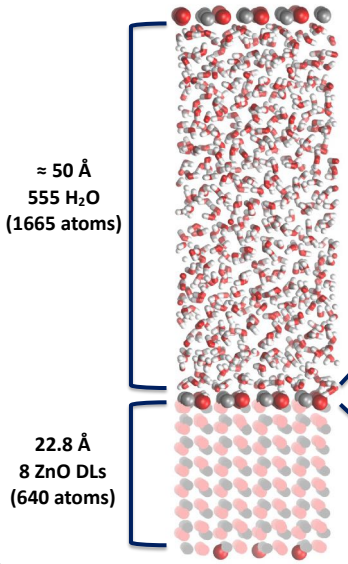
Water at ZnO(10$\bar{1}$0): System Setup

RUB

Slab (2305 atoms):

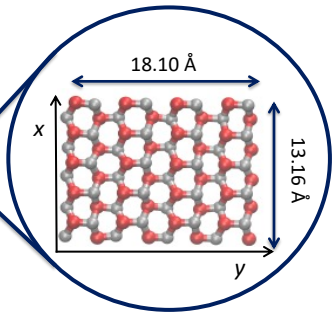


Equilibration in *z* (1 ns): 1 bar, 300 K

Production simulations: *NVT* (2 ns), 300 K

CPU time (per MD step): ≈ 3.3 core·s

(5 x 4) supercell:



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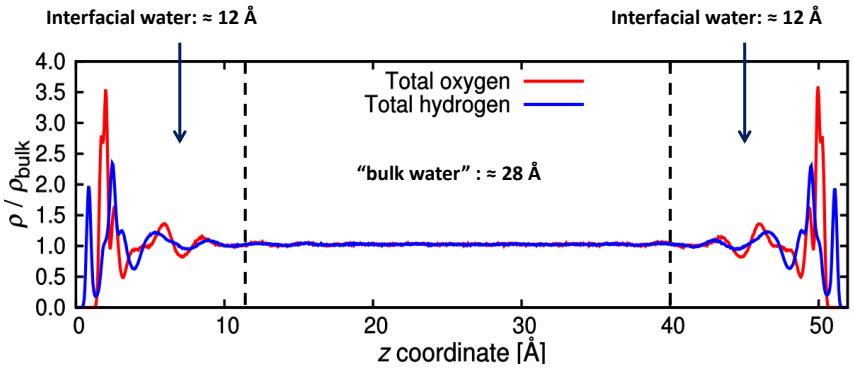
Water at ZnO(10$\bar{1}$0): System Size Convergence

RUB

Probability Distribution ρ:



⇒ System size is converged, bulk water in the central region

⇒ Peaks can be assigned to different species at the surface

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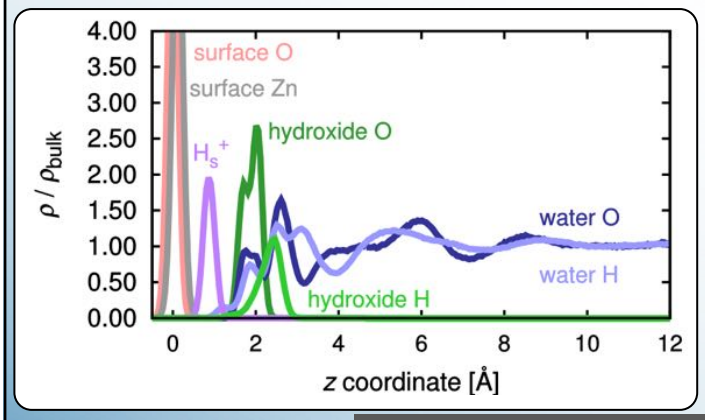
Water at ZnO(10$\bar{1}$0): Surface Species

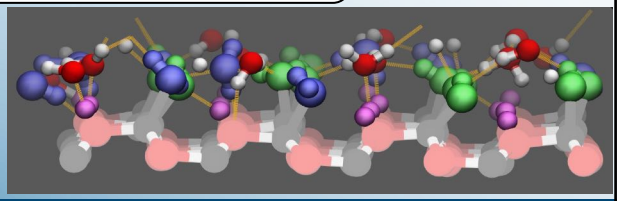
RUB



Water at the Surface:

Neutral H_2O: 27.7 %

Dissociated H_2O: 72.3 %

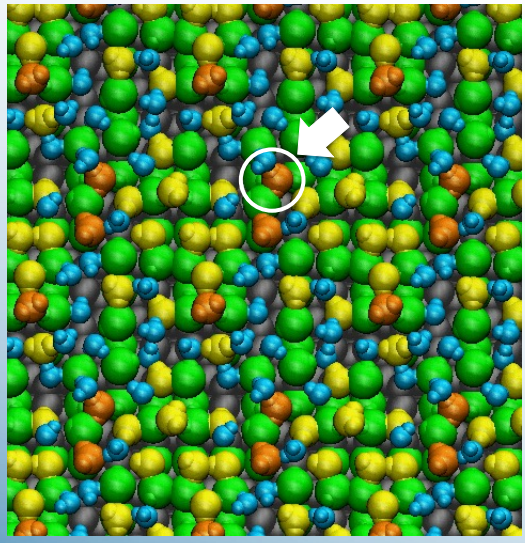


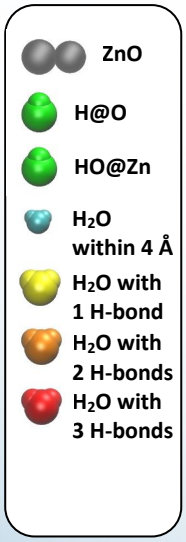
Jörg Behler Kiel 2023

65

Water at ZnO(10$\bar{1}$0): Water Dissociation and Surface Hydroxylation

RUB





Jörg Behler Kiel 2023

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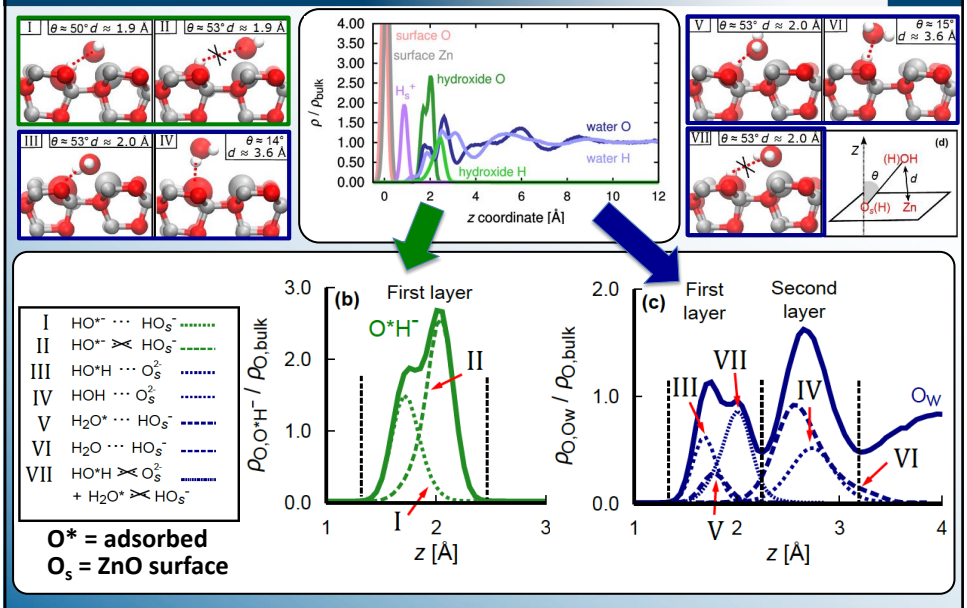
Water at ZnO(10$\bar{1}$0): Surface Species

RUB



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Water at ZnO(10$\bar{1}$0): Dissociation and Recombination Mechanisms

RUB

Molecular and dissociative adsorption

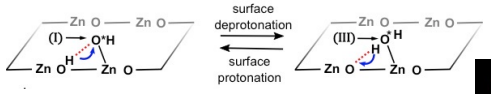
⇒ mixture of OH^-, H^+ and H_2O at the interface

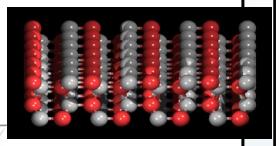
⇒ dynamic system, frequent interconversion processes

<u>Two Scenarios:</u> Water dissociation/recombination by proton transfer to/from

- surface oxide and hydroxide groups ⇒ "***surface PT***"

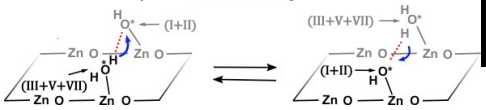
slow





- adsorbed hydroxide/water species ⇒ "***adlayer PT***"

fast



⇒ **both controlled by presolvation**

V. Quaranta, M. Hellström and J. Behler, *J. Phys. Chem. Lett.* **8** (2017) 1476.

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Water at ZnO(10$\bar{1}$0): Dissociation and Recombination Mechanisms

RUB

surface-PT

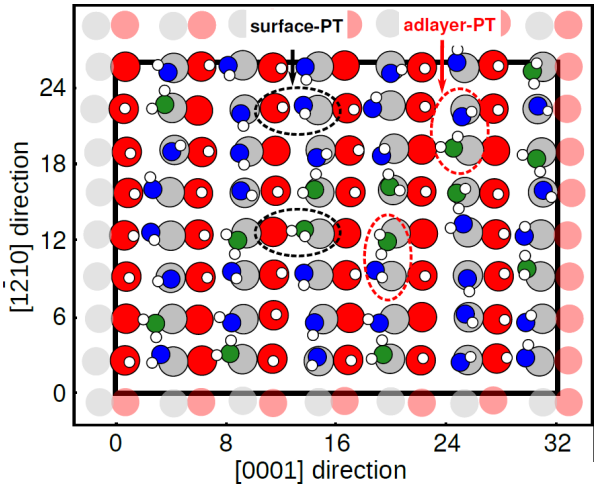
$O_SH^- \cdots O^*H^- \rightleftharpoons O_S^{2-} \cdots HO^*H$

slow

adlayer-PT

$HO^*H \cdots O^*H^- \rightleftharpoons HO^{*-} \cdots HO^*H$

fast

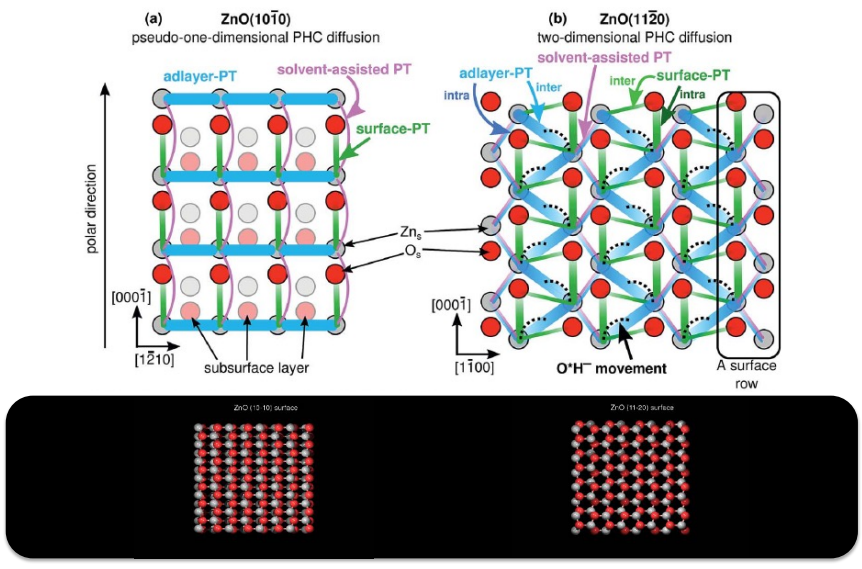


V. Quaranta, J. Behler, and M. Hellström, *J. Phys. Chem. C* **123** (2019) 1293.

69

Water at ZnO: 1D vs. 2D Proton Transport

RUB



M. Hellström, V. Quaranta, and J. Behler, Chem. Sci. **10** (2019) 1232.

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Summary: Four Generations of Neural Network Potentials

RUB

First-Generation Neural Network Potentials

Global description ⇒ low-dimensional systems

Second-Generation Neural Network Potentials

Short-range: yes Long-range: no Non-local: no Spin: yes

J. Behler, M. Parrinello, *Phys. Rev. Lett.* 98 (2007) 146401.

Third-Generation Neural Network Potentials

Short-range: yes Long-range: yes Non-local: no Spin: yes

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

Fourth-Generation Neural Network Potentials

Short-range: yes Long-range: yes Non-local: yes Spin: yes

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

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Neural Network Potentials fill a gap in the toolbox of chemistry, physics and materials science

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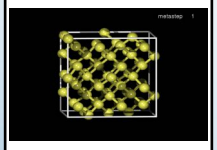
Summary: Applications of Neural Network Potentials

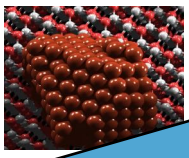
RUB

Bulk Materials



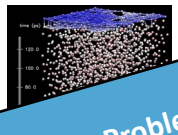
PRL 98 (2007) 146401.
PRL 100 (2008) 185501

Nanostructures

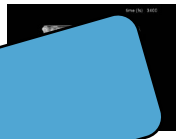


PRB [illegible]

Nucleation



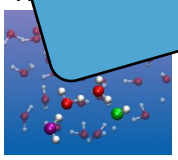
Phase Transitions



[illegible] 100103.
[illegible]ure Materials 10 (2011) 693.

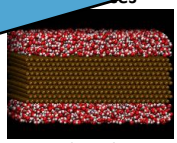
Neural Networks Help Solving Problems

P[illegible]



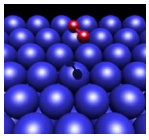
PNAS 113 (2016) 8368.

[illegible]



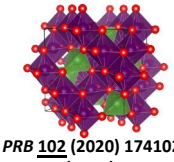
PCCP 18 (2016) 28704.
JPCC 121 (2017) 4368.

Gas-Surface Dynamics



JPCL 10 (2019) 2957.
JPCL 10 (2019) 1763.

Li-Intercalation Compounds



PRB 102 (2020) 174102.
JCP 153 (2020) 164107.

and many more …

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