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Constructing High-Dimensional Neural Network Potentials (NNPs) to Describe the Solvation of Protonated Water Clusters by Superfluid Helium

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How to simulate solutes in superfluid helium?

Ab initio/bosonic path integral MD/MC method (Marx Group, 2014)

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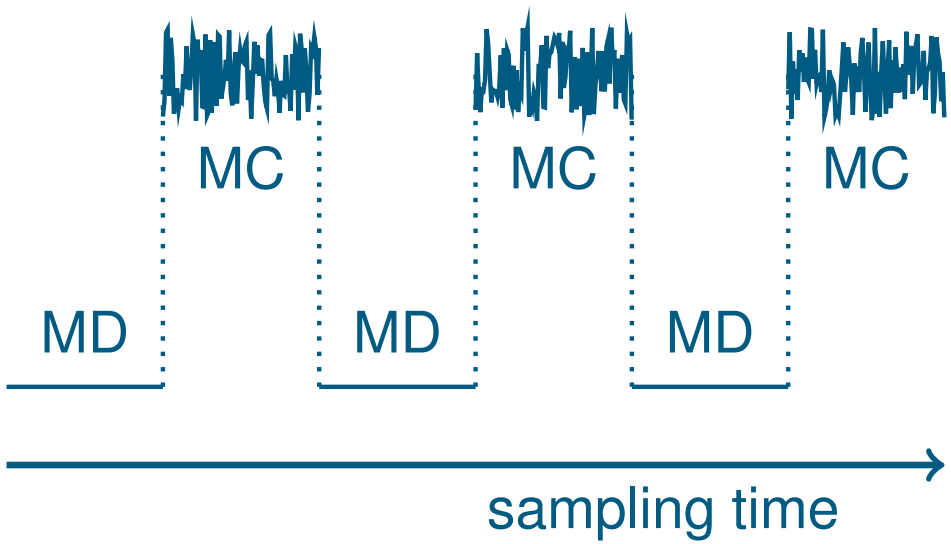
Superfluid ^{4}He

- Bosonic PIMC
- Pair-density matrix approximation[1]
- Aziz pair potential[2]

Reactive Solutes

- *Ab initio* PIMD (DFT)
- PIGLET[3] to account for low temperature ($\sim$1 K)

LaBerge-Tully[4] "mixed MD/MC method":



$\rightarrow$ He-solute coupling by pairwise additive **interaction potentials**

[1] *Rev. Mod. Phys.*, 1995, **67**, 279-355

[2] *JCP*, 1979, **70**, 4330-4342

[3] *Phys. Rev. Lett.*, 2012, **109**, 100604

[4] *Chem. Phys.*, 2000, **260**, 183-191

Goal

Represent pair-wise additive interaction potential

Relate coordinates to interaction energy

- Instead of physical functional form use HD-NNP[1] together with atom-centered symmetry functions[2] to describe chemical environment

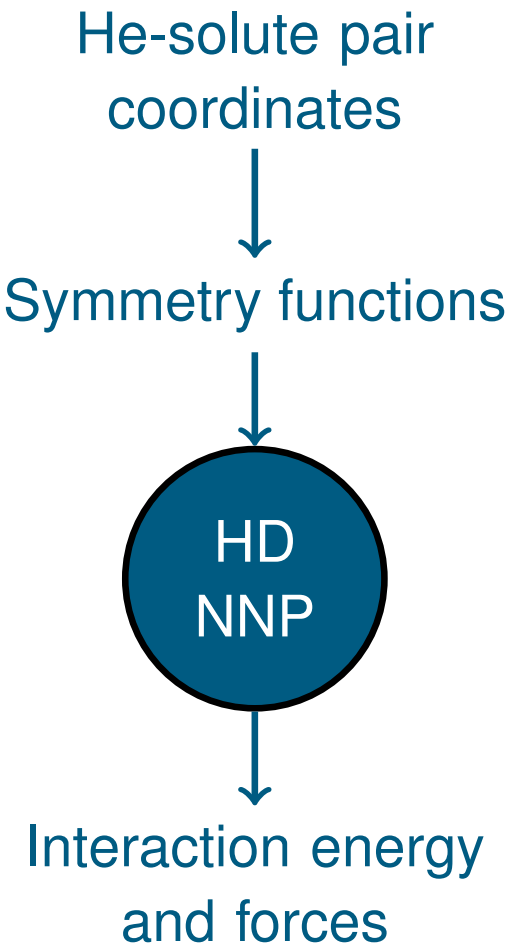
Obstacles

- Potential is evaluated many million times

→ Efficient evaluation required

- Potential needs to be highly accurate (He-He interaction: 0.1 kJ/mol)

→ CCSD(T)/AVTZcp (essentially converged)



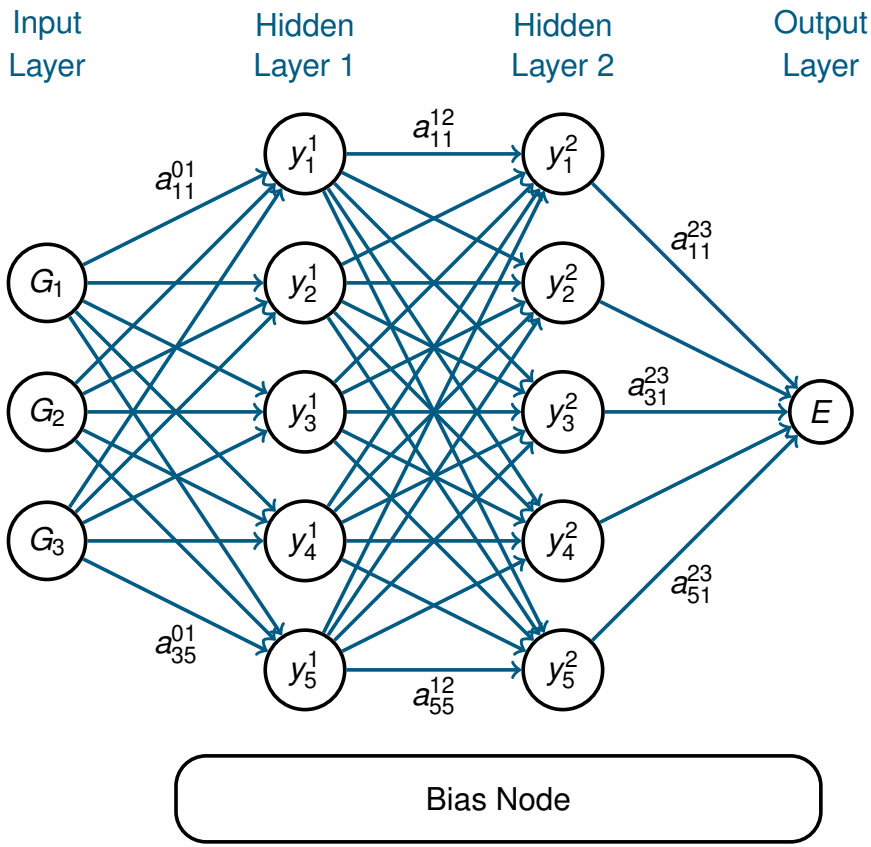
[1] *PRL*, 2007, **98**, 146401

[2] *JCP*, 2011, **134**, 074106

Neural Network Potentials

General structure

- Input (coordinates), hidden and output (energy) layers with **nodes** G, y, E
- Nodes connected by **weights** a to previous layer
- **Bias** node b connected to some nodes
- Activation function $f = \tanh(u)$
- Highly flexible functional form
- Has analytical derivative

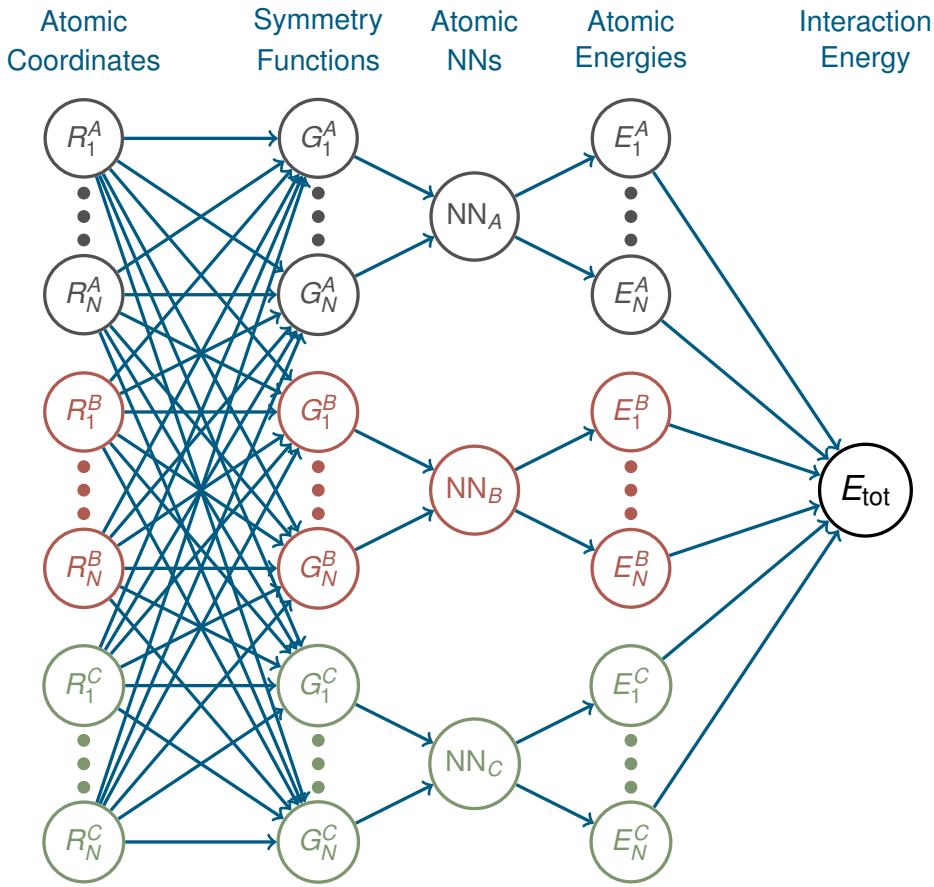


$$y = f\left(b + \sum_{\text{nodes}}^{\text{previous}} a_i \cdot x_i\right)$$

High-Dimensional Neural Networks

Concept[1,2]

- Atomic networks for each element
- Separate sets of symmetry functions to represent chemical environment
- Output is atomic contribution to total interaction energy
- Can be fitted to reference calculations by local optimization of the weight parameters



[1] *PRL*, 2007, **98**, 146401
[2] *Angew. Chemie Int. Ed.*, 2017,

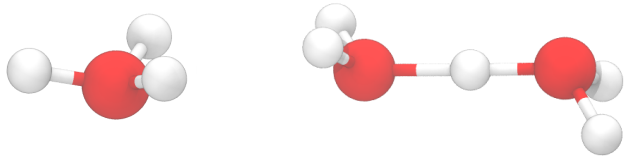
10.1002/anie.201703114

Generation of Reference Structures

Vacuum simulations of solutes

- 25 ps AI-PIMD trajectories with RPBE-D3/TZV2P at 1.67K, 48 replicas + PIGLET

→ Basis for He sampling positions



Hydronium Zundel

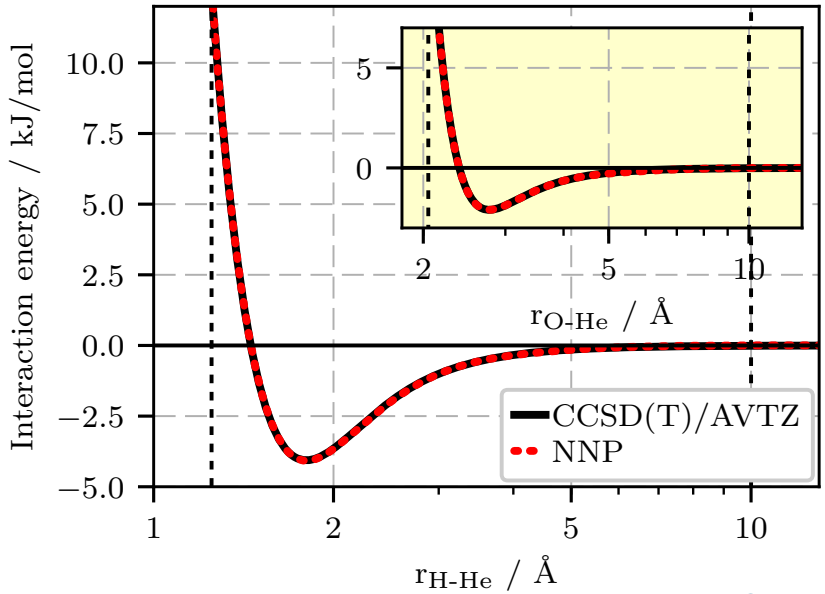
He-solute pair generation

- Euler-Maclaurin[1] radial grids
- Lebedev[2] angular grids

$$r_{\text{cut}} = \begin{cases} 2.05\ \text{Å} < r_{\text{O-He}} < 10.0\ \text{Å} \\ 1.25\ \text{Å} < r_{\text{H-He}} < 10.0\ \text{Å} \end{cases}$$

[1] *Mol. Phys.*, 1993, **78**, 997-1014

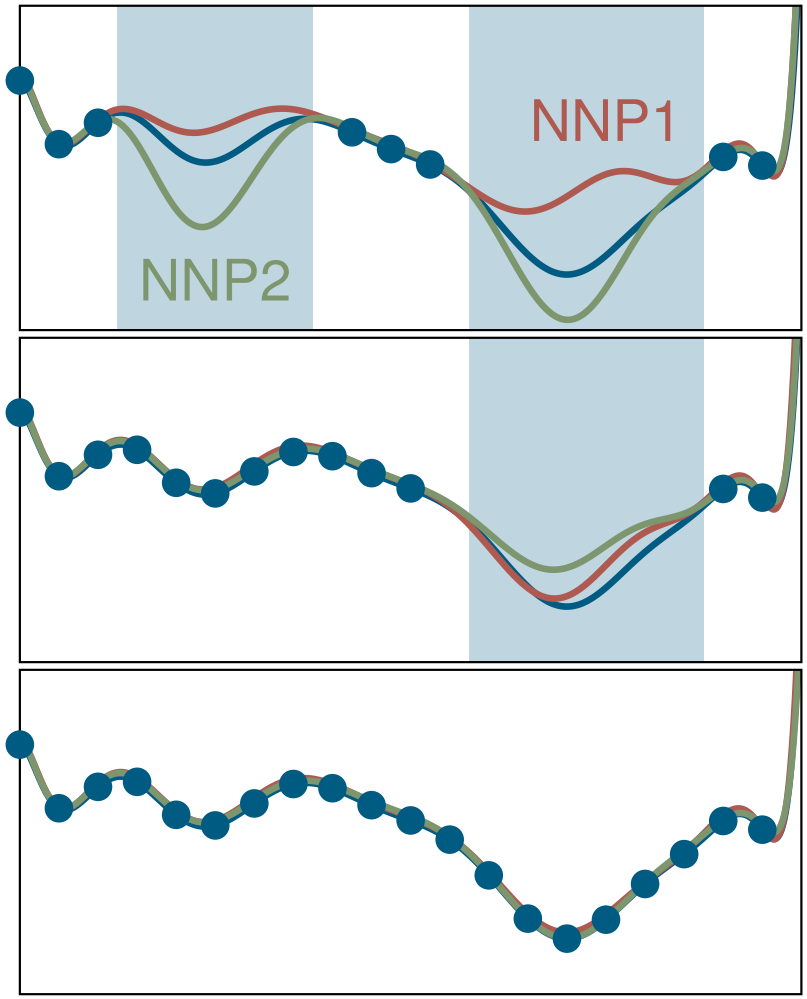
[2] *Sib. Math. J.*, 1977, **18**, 99-107



Iterative Improvement

Identify missing structures

1) Use flexibility to your advantage:
   - 2 NNPs with different setup
   - Generate new He-solute pairs
   - Identify structures with large ΔE
2) Include He solvation effect:
   - Run simulations of flexible solutes in bulk helium
   - Identify structures outside range of symmetry functions of training set



Final He-Solute NNPs

He-hydronium:

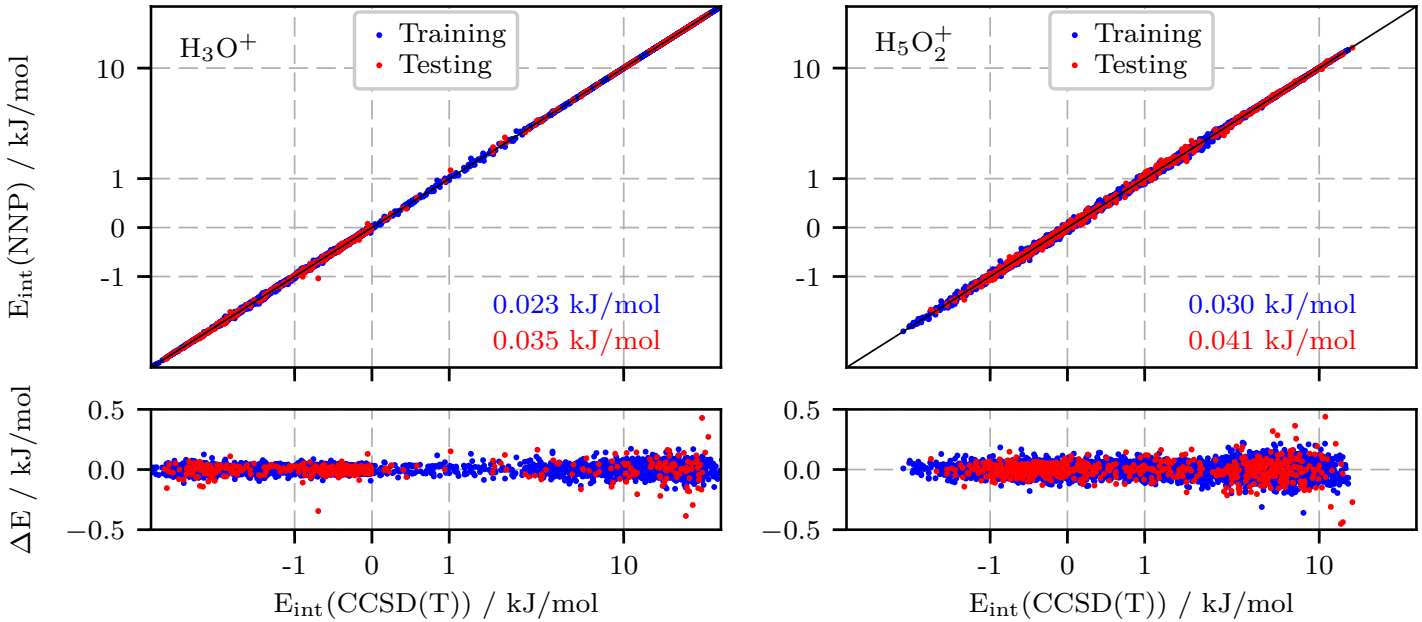
1) 12 refining stages (1000 new structures each)
2) 3545 structures from He-bulk

= 15545 CCSD(T)/AVTZcp reference calculations

He-Zundel:

1) 21 refining stages (1000 new structures each)
2) 4101 structures from He-bulk

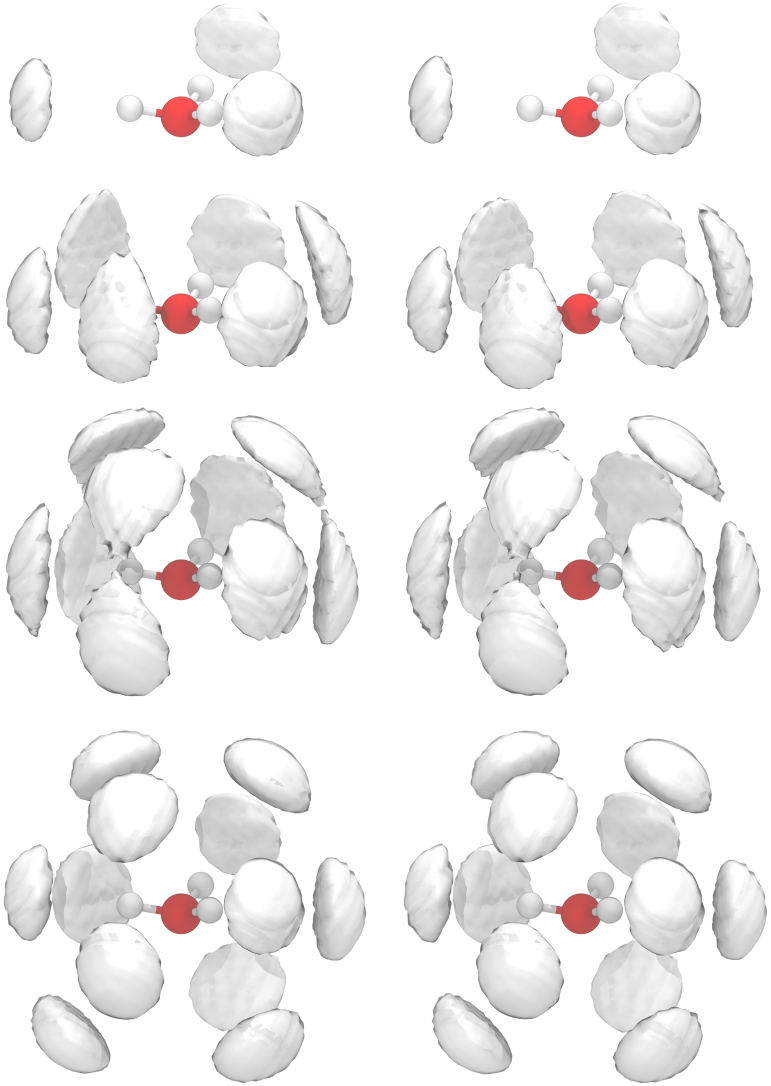
= 25101 CCSD(T)/AVTZcp reference calculations



He-Hydronium Microsolvation

Validation of NNPs

- Evaluate potential on grid with CCSD(T) and NNP for selected frozen solute configurations[1]
- Simulate helium around frozen configurations where interaction energy is used from nearest grid point
- Compare spatial distribution functions for different number of helium atoms (3,6,10,14)



CCSD(T) grid NNP grid

[1] *PCCP*, 2017, **19**, 8307-8321

Hydronium Cation in Bulk Helium

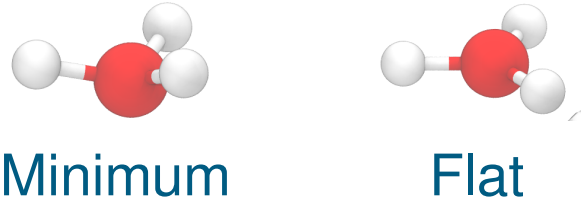
Details

- 98 helium atoms around frozen hydronium configuration in truncated octahedron
- NNP and CCSD(T) grid for He-solute interaction

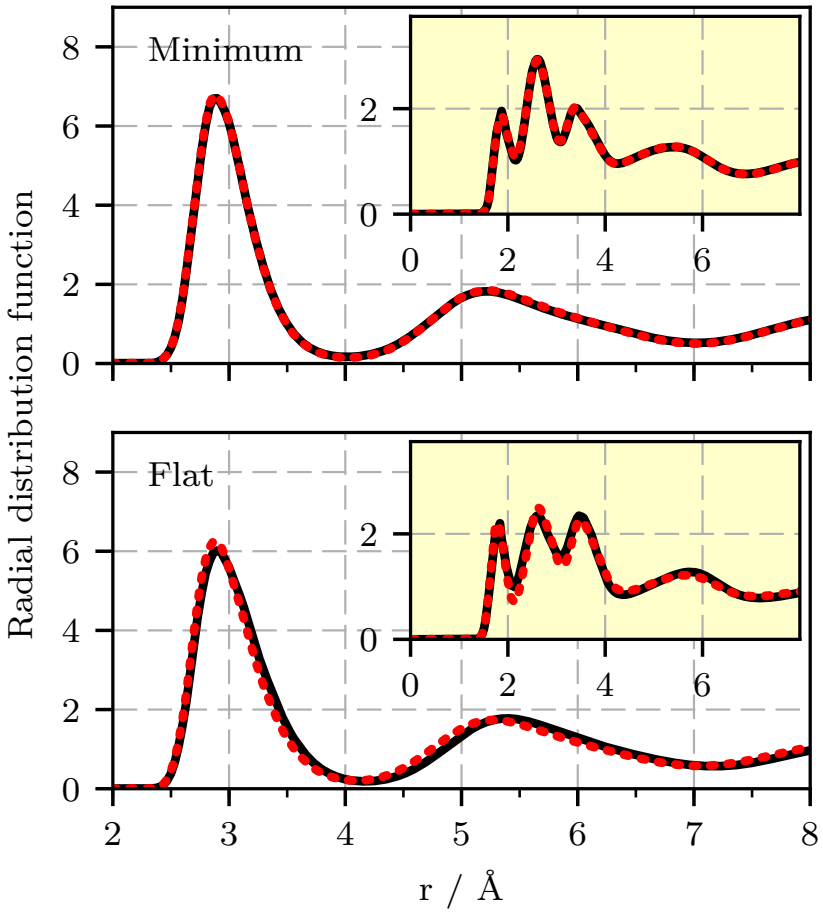
→ Almost perfect agreement in RDFs

→ Well structured solvation shells

→ Almost no migration between shells



Minimum Flat



Zundel Cation in Bulk Helium

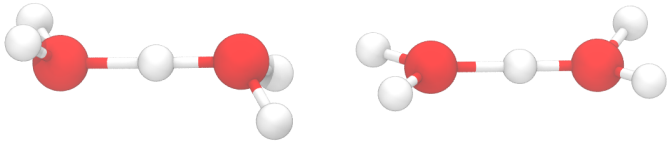
Details

- 88 helium atoms around frozen Zundel configuration in truncated octahedron
- NNP and CCSD(T) grid for He-solute interaction

→ Almost perfect agreement in RDFs

→ Broader peaks compared to He-hydronimum

→ Smaller interaction due to charge delocalization



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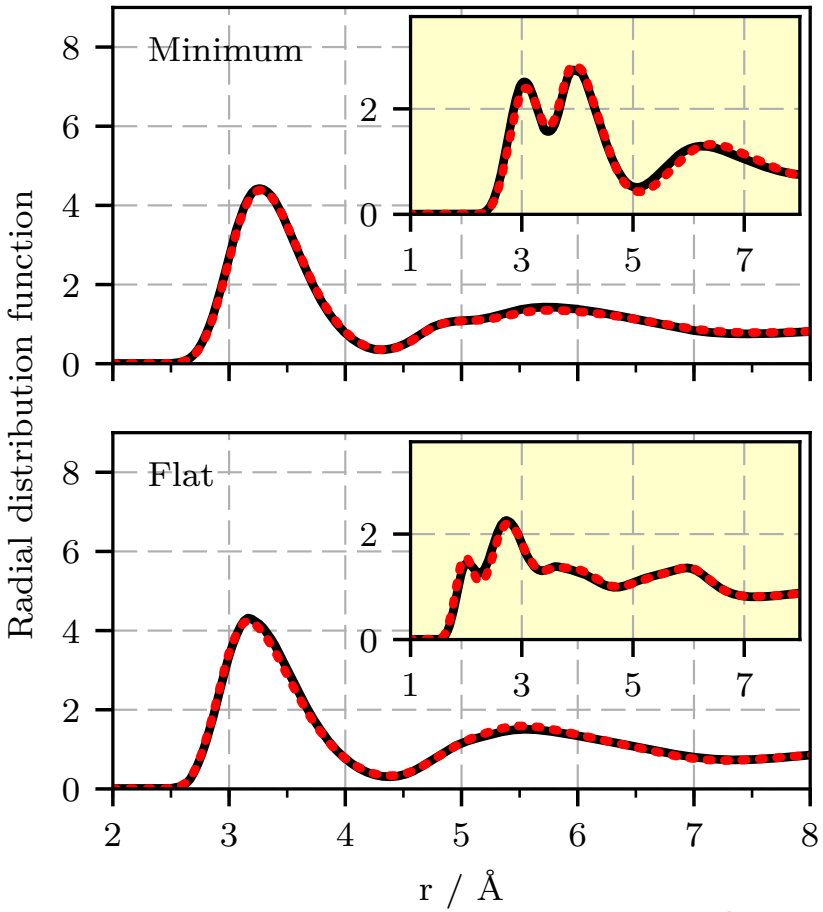

Summary & Future Directions

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Summary

- Systematic and automated procedure to develop pair-wise additive He-solute interaction potentials
- Convincing agreement with CCSD(T)/AVTZcp
- NN properties allow to substantially reduce number of reference calculations

Outlook

- Study stepwise microsolvation up to bulk helium for flexible solutes
- Extend to other solutes in different quantum solvents (e.g. p-H_2)
- Apply HD-NNPs for other simulation techniques (QM/MM)

Acknowledgment

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- Felix Uhl and Harald Forbert
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FCI FONDS DER CHEMISCHEN INDUSTRIE

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Feed Forward Neural Networks

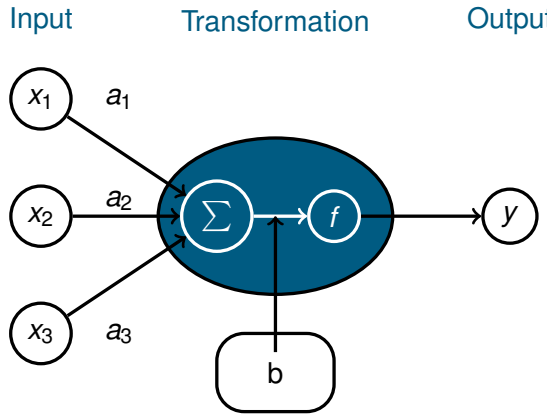
Multi-layer perceptron

Calculation of node value y

- Multiply all input values x_i from previous layer by weight a_i
- Sum up products
- Add bias weight b
- Apply activation function f

Activation function introduces flexibility
Otherwise: Linear dependence on previous layer

$$f(u) = \tanh(u)$$



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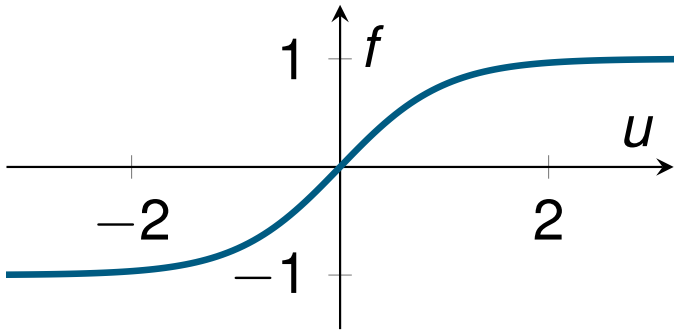

Symmetry Functions

Fingerprint of chemical environment

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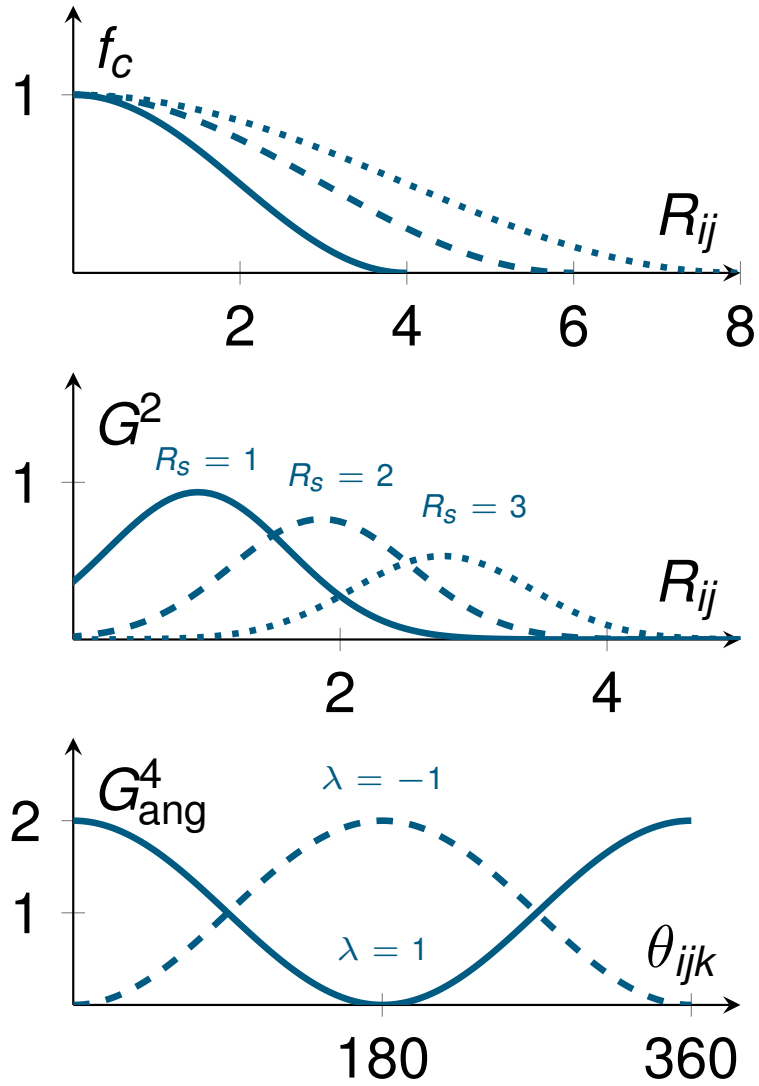
Transformation of coordinates[1]

$$f_c(R_{ij}) = \begin{cases} \frac{1}{2}\cos\left(\frac{\pi R_{ij}}{R_c}\right) + \frac{1}{2} & R_{ij} \leq R_c \\ 0 & \text{else} \end{cases}$$

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

$$G_i^4 = 2^{1-\zeta} \sum_{j,k\neq i} (1+\lambda\cos\theta_{ijk})^\zeta \cdot e^{-\eta(R_{ij}^2+R_{ik}^2+R_{jk}^2)} \cdot f_c(R_{ij}) \cdot f_c(R_{ik}) \cdot f_c(R_{jk})$$



[1] *JCP*, 2011, **134**, 074106

High-Dimensional Neural Networks

How to fit?

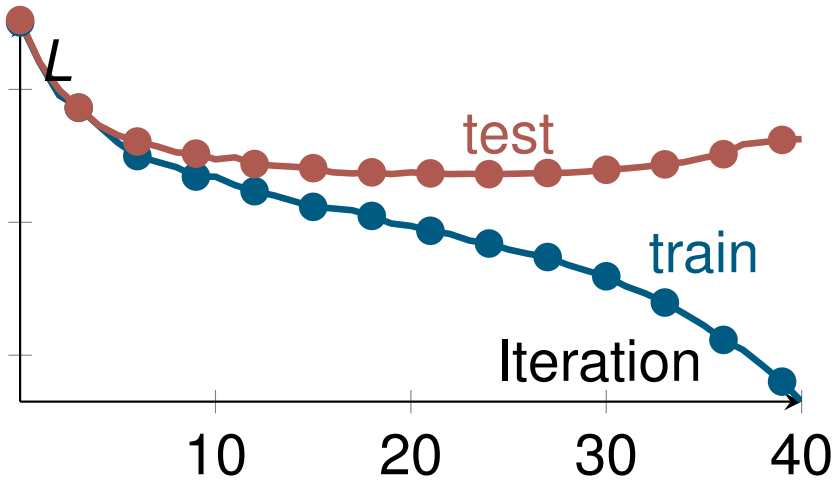
Minimize loss (locally)

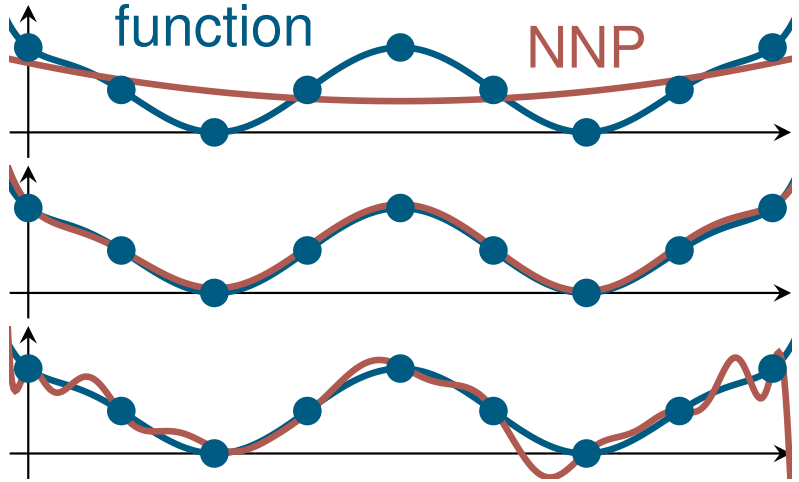
$$E_{\text{tot}}^{\text{NN}} = \sum_{i=1}^{\text{ele}} \sum_{j=1}^{\text{natom}_i} E_{\text{NN}_i}^{j}$$

$$L = \frac{1}{N} \sum_{n=1}^{N} \left(E_{(i,\text{tot})}^{\text{ref}} - E_{(i,\text{tot})}^{\text{NN}} \right)^2$$

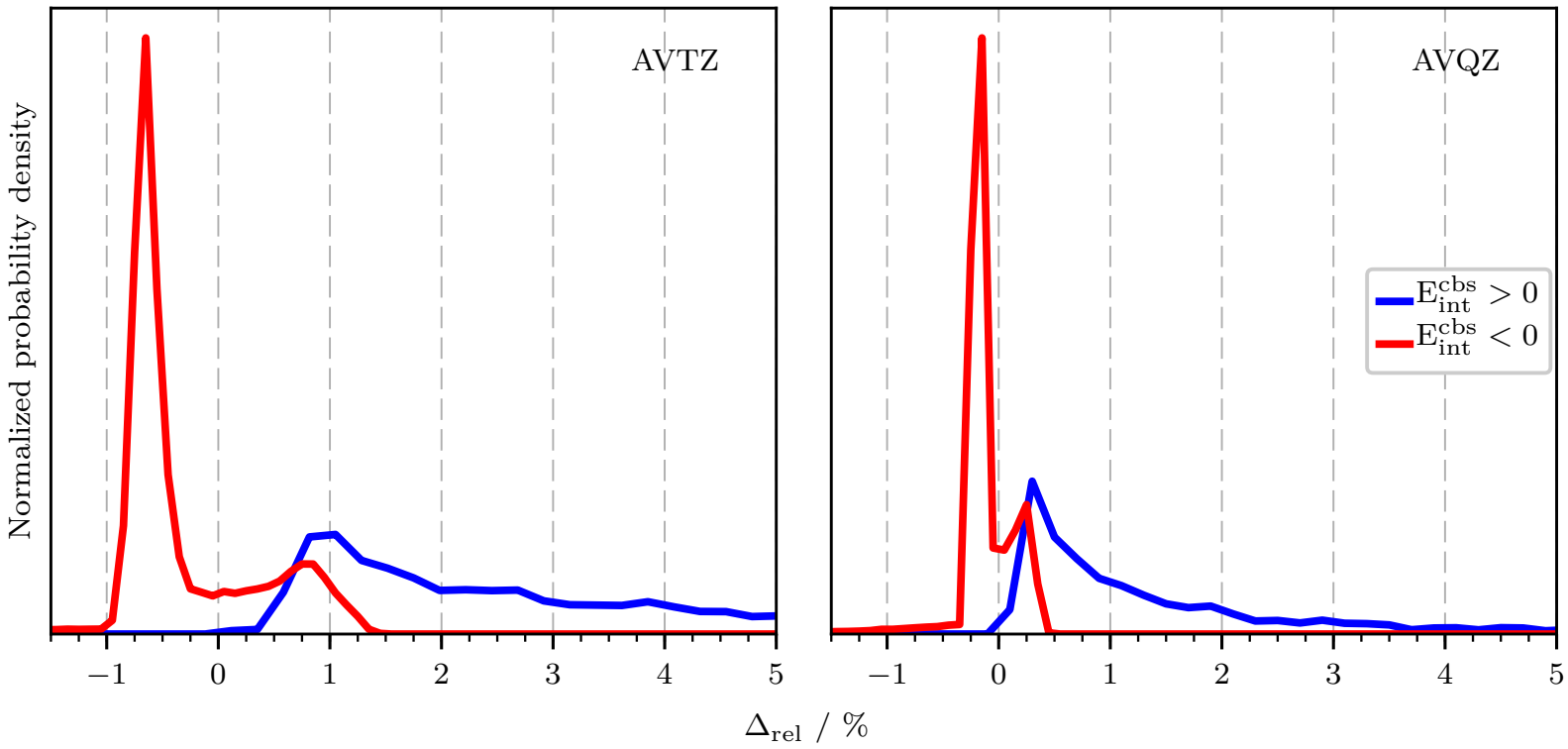
- L is function of weights w
- Minimize L by changing w
- e.g. steepest decent:

$$w_{\text{new}} = w_{\text{old}} - \gamma \frac{\partial}{\partial w} L(w)$$





Basis Set Convergence Tests for Reference Calculations



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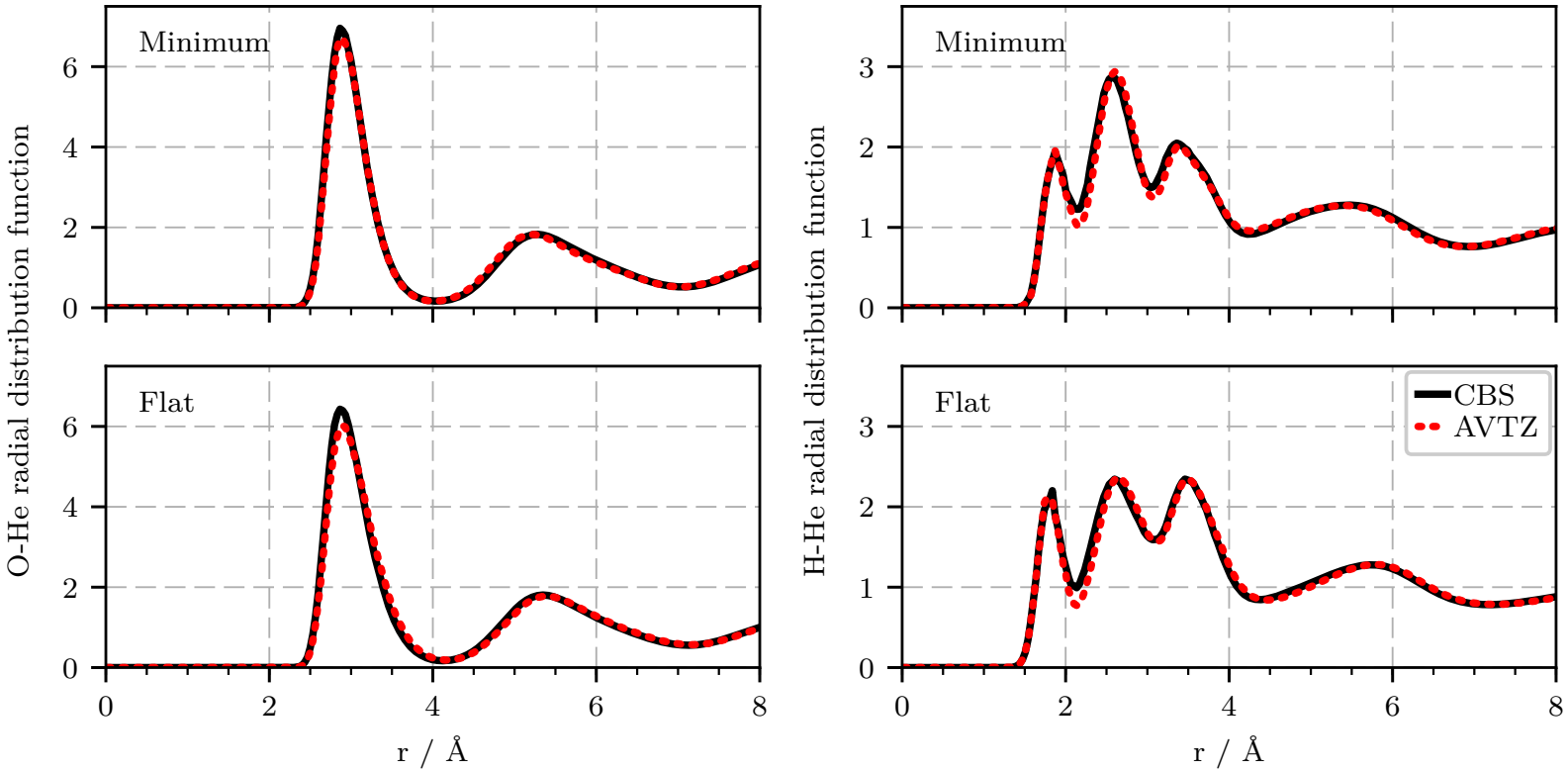

Box Convergence Tests for Bulk Helium