



UNIVERSITÄT  
BAYREUTH



FRITZ-HABER-INSTITUT  
MAX-PLANCK-GESELLSCHAFT

# Charge Equilibration in Machine Learning Potentials

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19.3.2025

# Why?

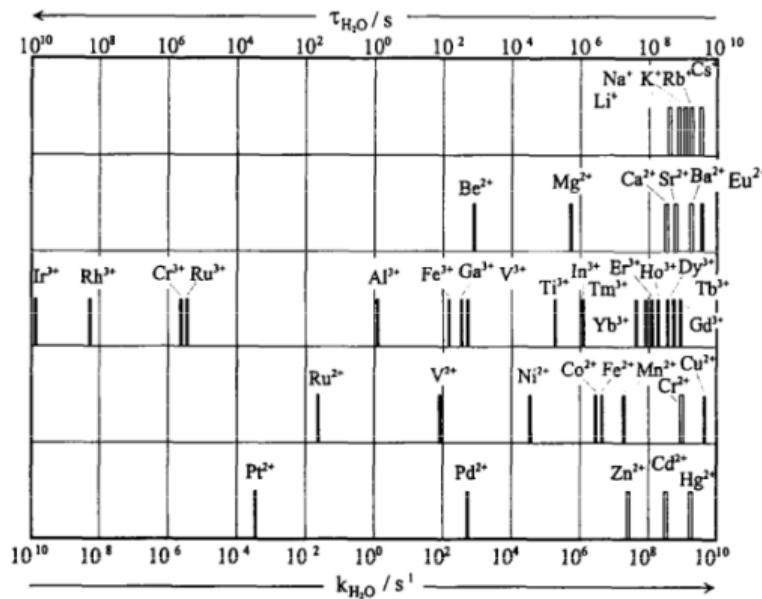
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1) L. Helm, et.al. Water exchange on metal ions: experiments and simulations. *Coordination Chemistry Reviews*. 187(1), 1999

2) K. L. Milton, et.al. Difference in Structure and Electronic Properties of Oxygen Vacancies in  $\alpha$ -Quartz and  $\alpha$ -Cristobalite Phases of  $\text{SiO}_2$ . *Materials*, 16(3), 2023

# Why?

## 1) Lifetime of water in the solvation layer

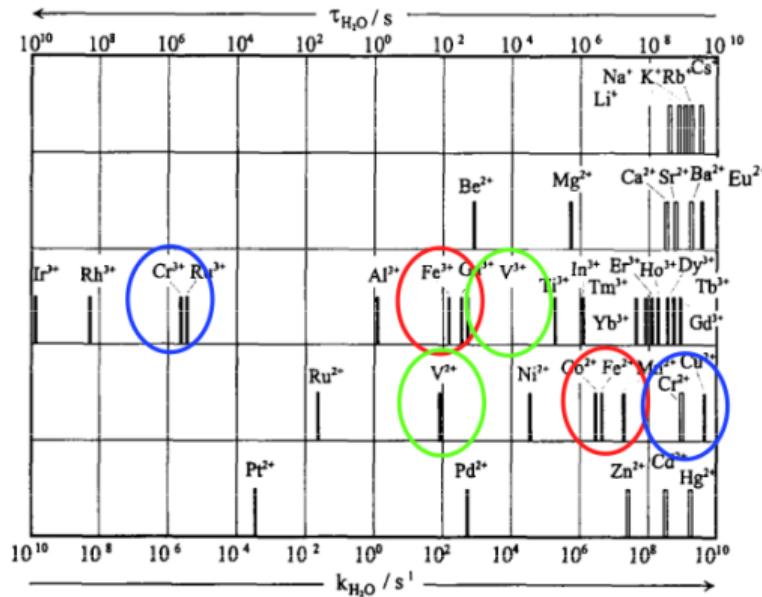


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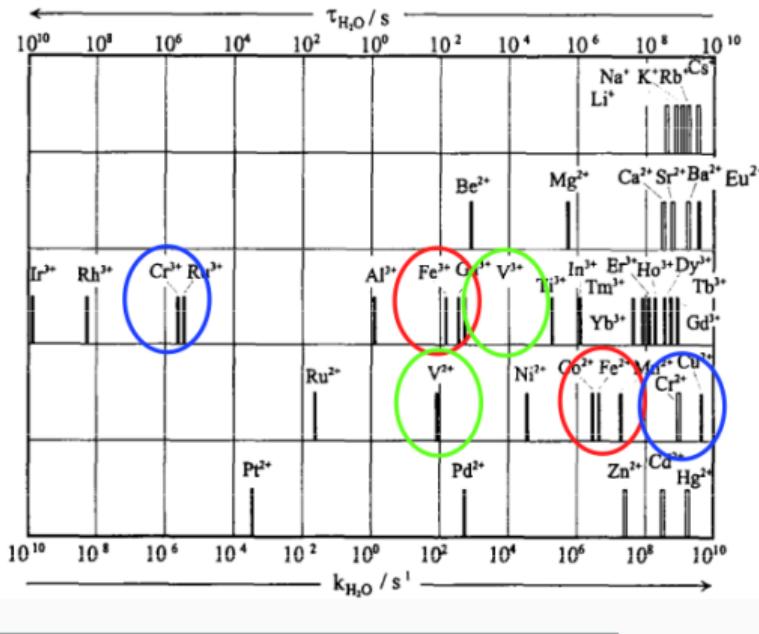


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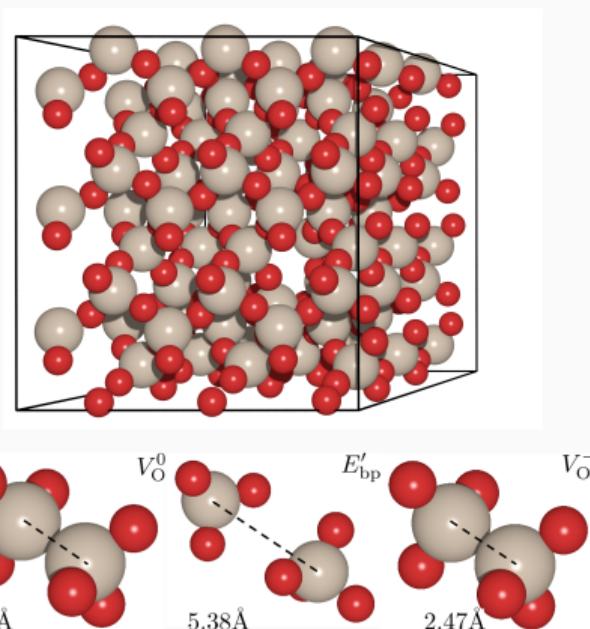
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# Why?

## 1) Lifetime of water in the solvation layer



## 2) Charge defects in $SiO_2$



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## Charge Equilibration

$$E_{\text{tot}} \approx E_{\text{short}} + E_{\text{QEq}} = E_{\text{short}} + \underbrace{\sum_{i=1}^N \left( \chi_i q_i + \frac{1}{2} J_i q_i^2 \right)}_{\text{$\chi$ - electronegativity}} + \underbrace{\frac{1}{2} \iint \frac{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'}_{\text{Coulomb-Integral}}$$

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$\chi$  - electronegativity

$$\min_{\mathbf{q}} E_{\text{QEq}}, \sum_i^N q_i = Q_{\text{tot}}$$

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## 1) Closed form

$$\begin{pmatrix} A_{1,1} & A_{1,2} & \cdots & A_{1,N} & 1 \\ A_{2,1} & A_{2,2} & \cdots & A_{2,N} & 1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ A_{N,1} & A_{N,2} & \cdots & A_{N,N} & 1 \\ 1 & 1 & \cdots & 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} q_1 \\ q_2 \\ \vdots \\ q_N \\ \lambda \end{pmatrix} = - \begin{pmatrix} \chi_1 \\ \chi_2 \\ \vdots \\ \chi_N \\ -q_{\text{tot}} \end{pmatrix}$$

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2) **Iteratively minimize with gradient descent**

# QE<sub>q</sub> External Field

$$E_{\text{QE}q} = \underbrace{\sum_{i=1}^N \left( \chi_i q_i + \frac{1}{2} J_i q_i^2 \right)}_{\text{Site-Energy}} + \underbrace{\frac{1}{2} \iint \frac{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'}_{\text{Coulomb-Integral}} - \underbrace{\sum_{i=1}^N \left( q_i \sum_{\mu=1}^3 (r_{i\mu} \epsilon_{\mu}) \right)}_{\text{External-Field}}$$

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$$\begin{pmatrix} A_{1,1} & A_{1,2} & \cdots & A_{1,N} & 1 \\ A_{2,1} & A_{2,2} & \cdots & A_{2,N} & 1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ A_{N,1} & A_{N,2} & \cdots & A_{N,N} & 1 \\ 1 & 1 & \cdots & 1 & 0 \end{pmatrix} \cdot \begin{pmatrix} q_1 \\ q_2 \\ \vdots \\ q_N \\ \lambda \end{pmatrix} = - \begin{pmatrix} \chi_1 - \mathbf{R}_1^T \boldsymbol{\epsilon} \\ \chi_2 - \mathbf{R}_2^T \boldsymbol{\epsilon} \\ \vdots \\ \chi_N - \mathbf{R}_N^T \boldsymbol{\epsilon} \\ -Q_{\text{tot}} \end{pmatrix}$$

## QE<sub>q</sub> in Machine Learning

Instead of **element**-dependent  $\chi(\mu)$ , ML-QE<sub>q</sub> introduces **environment**-dependent  $\chi(r)$

## Gaussian Process Regression

- Local ML - GAP
- QE<sub>q</sub> - kQE<sub>q</sub>

$$\chi_i(\mathbf{x}_i) = \sum_{m=1}^M k(\mathbf{x}_i, \mathbf{x}_m) w_m$$

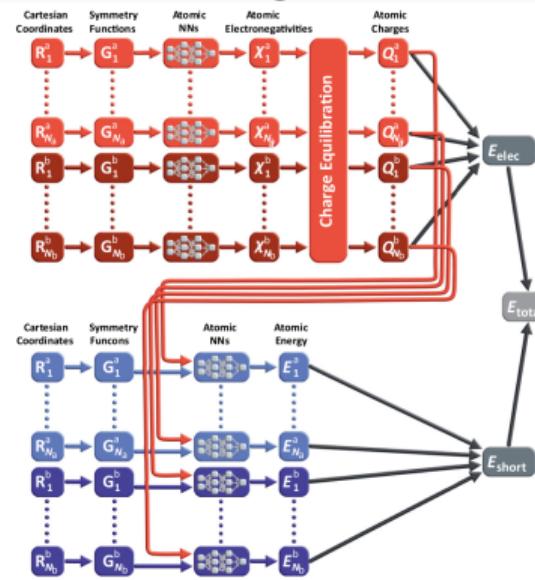
# QE in Machine Learning

## Gaussian Process Regression

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## 4th Generation High-Dimensional NN



1) T. W. Ko, et al. A fourth-generation high-dimensional neural network potential with accurate electrostatics including non-local charge transfer. *Nat Commun* 12(398) 2021

2) M. Gubler, et al. Accelerating Fourth-Generation Machine Learning Potentials Using Quasi-Linear Scaling Particle Mesh Charge Equilibration. *J. Chem. Theory Comput.* 2024

3) E. Kocer, et al.. Machine learning potentials for redox chemistry in solution, *arXiv* 2024

4) E. Kocer, et al.. Iterative charge equilibration for fourth-generation high-dimensional neural network potentials, *arXiv* 2025

# QEq in Machine Learning

## Gaussian Process Regression

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## 4th Generation High-Dimensional NN

- $\chi_i \propto \text{NN}(r_i) \rightarrow q_i$
- $E_i \propto \text{NN}(r_i, q_i)$

## Charge Constraint ACE

- PACE
- Equivariant

$$\chi_i \propto \sum_{nlm} \tilde{c}_{nlm} \mathbf{A}_{inlm}$$

# QE<sub>q</sub> in Machine Learning

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## MACE-QE<sub>q</sub>

- Equivariant Message Passing NN

$$\mathcal{R}^{(s)}(\mathbf{h}_i^{(s)}) = \begin{cases} \sum_k W_k^{(s)} h_{i,k00}^{(s)} & \text{if } s < S \\ \text{MLP} \left( \{h_{i,k00}^{(s)}\}_k \right) & \text{if } s = S \end{cases}$$

$$\chi_i(\mathbf{h}_i) = \mathcal{R}^{(s)} \left( \mathbf{h}_i^{(s)} \right)$$

# QE<sub>q</sub> in Machine Learning

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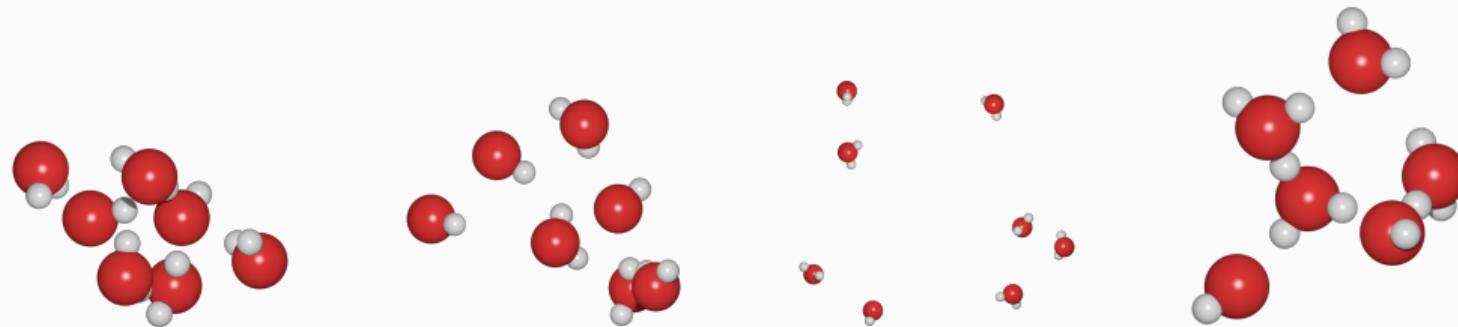
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# Water Cluster Dataset

- Water clusters of 3 to 10 molecules
- $Q_{\text{tot}} \in -1, 0, 1$
- Volumes scaled by factors  $D \in (0.9, 5.0)$
- FHI-Aims, PBE0 *tight* settings



# Gaussian Proces Regresion

- Gaussian Approximation Potential + Kernel Charge Equilibration

**GAP:**

$$E_{\text{short}} = \sum_{i=1}^{N_{at}} \epsilon(\mathbf{x}_i) = \sum_{i=1}^{N_{at}} \sum_{m=1}^M w_m^{\text{GAP}} k(\mathbf{x}_i, \mathbf{x}_m)$$

**kQE<sub>q</sub>:**

$$\chi(\mathbf{x}_i) = \sum_{m=1}^M w_m^{\text{kQE}_q} k(\mathbf{x}_i, \mathbf{x}_m)$$

# Gaussian Proces Regresion

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**kQE<sub>q</sub>:**

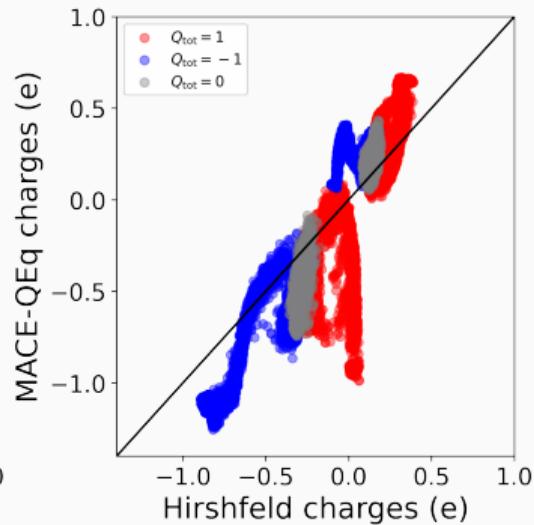
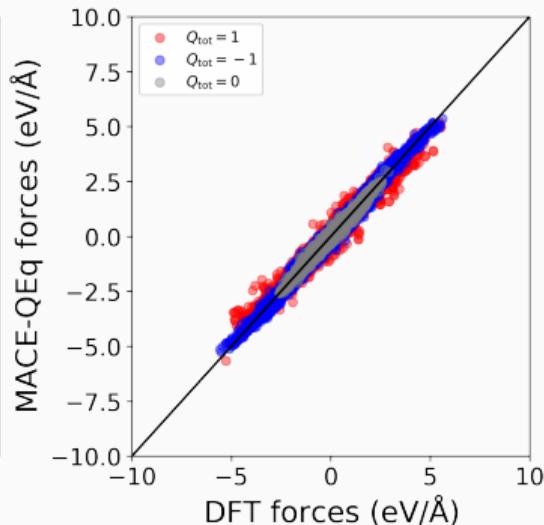
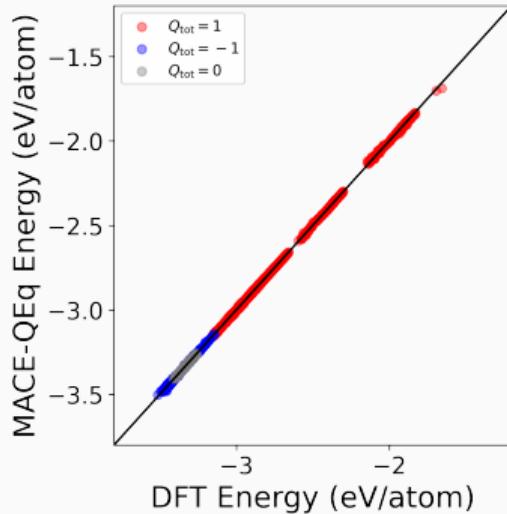
$$\chi(\mathbf{x}_i) = \sum_{m=1}^M w_m^{\text{kQE}_q} k(\mathbf{x}_i, \mathbf{x}_m)$$

Minimize loss function w.r.t. weights:  $\frac{\partial \mathcal{L}}{\partial w}$

$$\begin{bmatrix} \mathbf{w}_{t_1}^{\text{GAP}} \\ \mathbf{w}_{t_1}^{\text{kQE}_q} \end{bmatrix} = \left( \begin{bmatrix} \mathbf{K}_{MM}^{\text{GAP}} & 0 \\ 0 & \mathbf{K}_{MM}^{\text{kQE}_q} \end{bmatrix} + (\mathbf{LK})\boldsymbol{\Sigma}^{-1}(\mathbf{LK})^T \right)^{-1} ((\mathbf{LK})\boldsymbol{\Sigma}^{-1} (\mathbf{p}_{t_1} - \mathbf{y}_{t_1}))$$

# GAP+kQE<sub>q</sub> Water Clusters

- Water clusters (3-10 molecules)
- GAP + kQE<sub>q</sub> model fitted on  $E$ , and  $F$



- Multi-ACE
- Message-Passing NN with almost no non-linearities

$$h_{i,k}^{(s+1)} \propto \sum_{\tilde{k}} W_{k\tilde{k}}^{(s)} m_{i,\tilde{k}}^{(s)} + \sum_{i,\tilde{k}} W_{k\tilde{k}}^{(s)} h_{i,\tilde{k}}^{(s)}$$

$$\mathcal{R}^{(s)}(\mathbf{h}_i^{(s)}) = \begin{cases} \sum_k W_k^{(s)} h_{i,k00}^{(s)} & \text{if } s < S \\ \text{MLP} \left( \{h_{i,k00}^{(s)}\}_k \right) & \text{if } s = S \end{cases}$$

MACE energy:

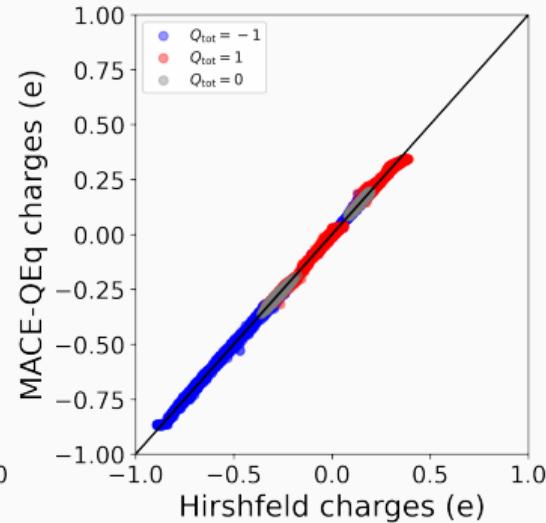
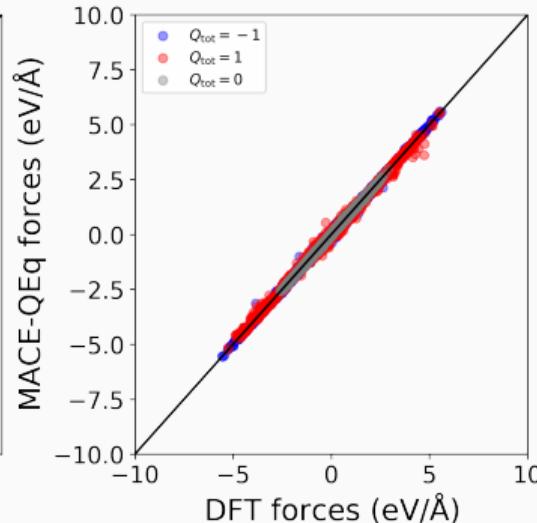
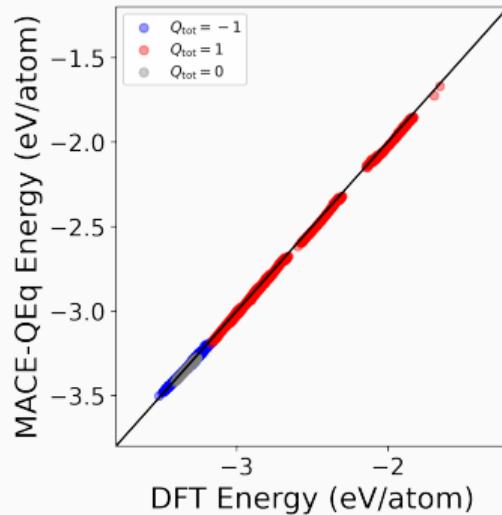
$$E_{\text{short}} = \sum_{i=0}^{N_{\text{at}}} \epsilon_i(\mathbf{h}_i) = \mathcal{R}_E^{(s)} \left( \mathbf{h}_i^{(s)} \right)$$

MACE-QEq electronegativities:

$$\chi_i(\mathbf{h}_i) = \mathcal{R}_{\chi}^{(s)} \left( \mathbf{h}_i^{(s)} \right)$$

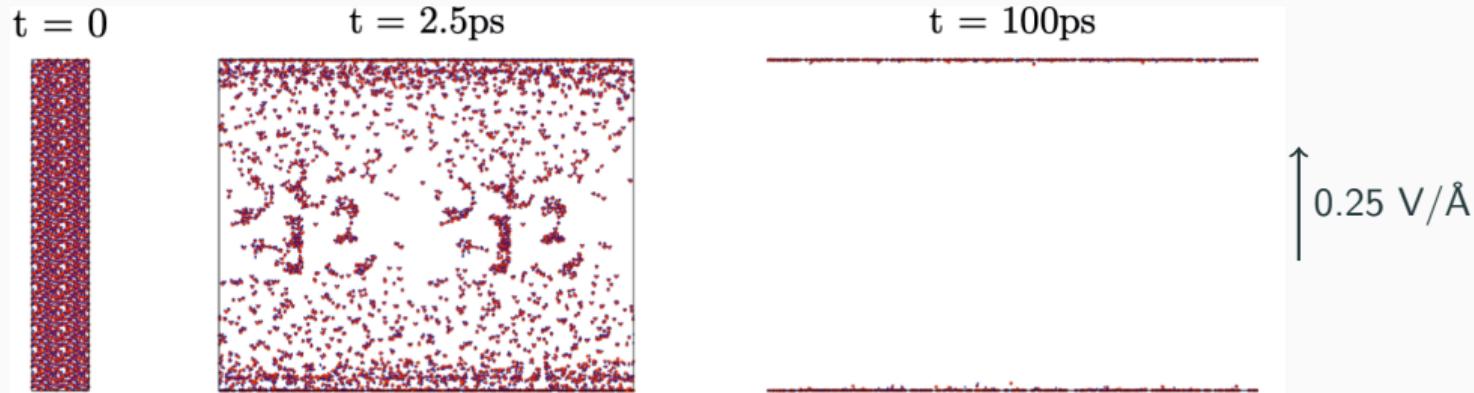
# MACE-QEq Water Clusters

- Water clusters (3-10 molecules)
- Fitted on  $E$ ,  $F$ , and Hirshfeld charges
- $128 \times 0e + 128 \times 1o$  MACE-QEq model



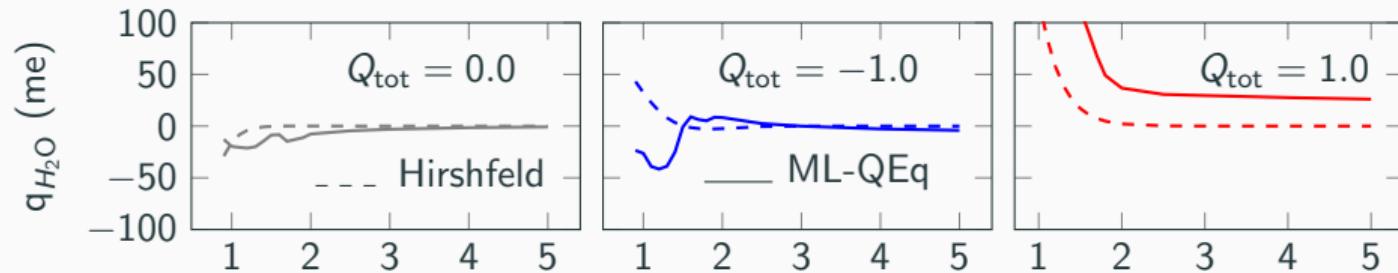
## Limitations of QEq

- Metallic-like behaviours
- Quadratic form is still limited - when discontinuous electron density as a function of geometry

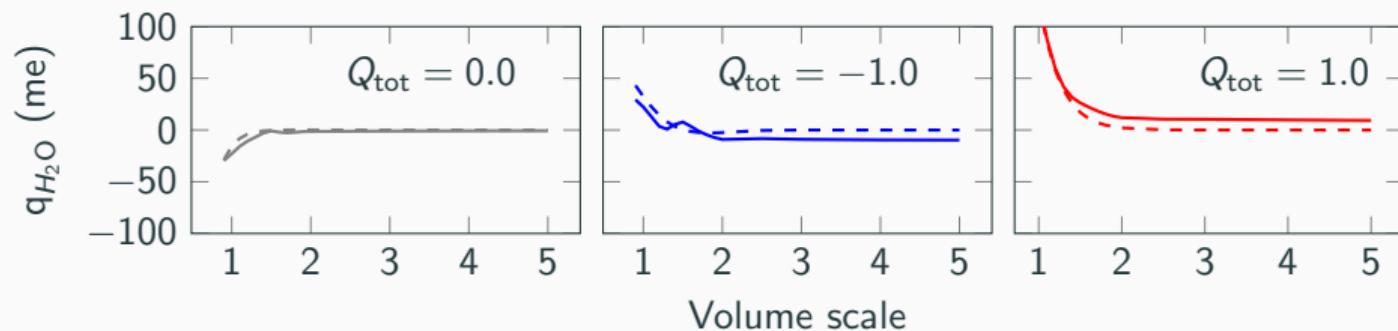


## Charges of scaled water clusters

GAP + kQE<sub>Eq</sub> model fitted to  $E$  and  $F$

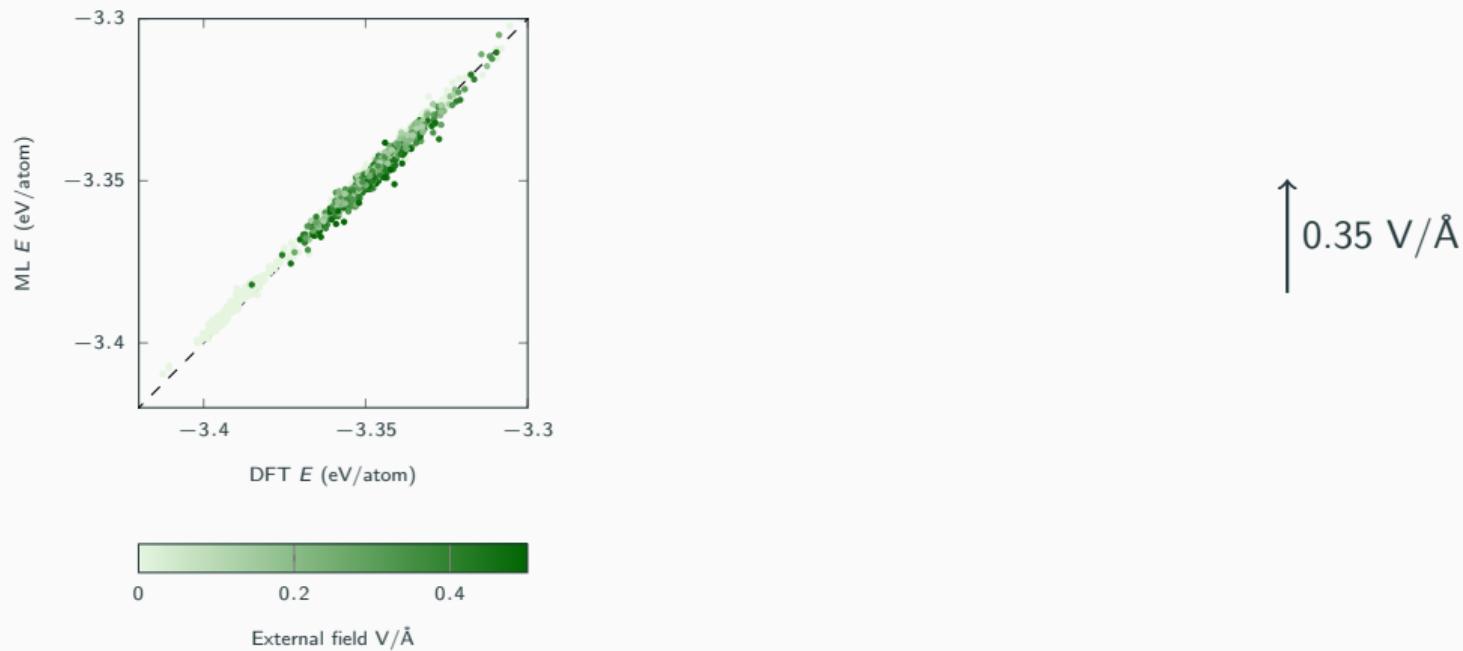


MACE-QEe model fitted to  $E$ ,  $F$ , and  $q$



# ML-QEq External Field

- Neutral water molecules
- GAP+kQE<sub>Q</sub>
- External fields  $\epsilon \in (0.1, 0.5) \text{ V}/\text{\AA}$



**GAP+kQE<sub>q</sub> code**



**kQE<sub>q</sub> paper**



**GAP+kQE<sub>q</sub> paper**

Almost done

**MACE-QE<sub>q</sub> code and paper**

Hopefully soon public



If you want something not public, write me an email [vondrak@fhi-berlin.mpg.de](mailto:vondrak@fhi-berlin.mpg.de), but there is often no documentation

GAP + kQE<sub>q</sub> model fitted to  $E$  and  $F$