



UNIVERSITÄT
BAYREUTH



FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

Charge Equilibration in Machine Learning Potentials

Martin Vondrák, Johannes T. Margraf, Karsten Reuter

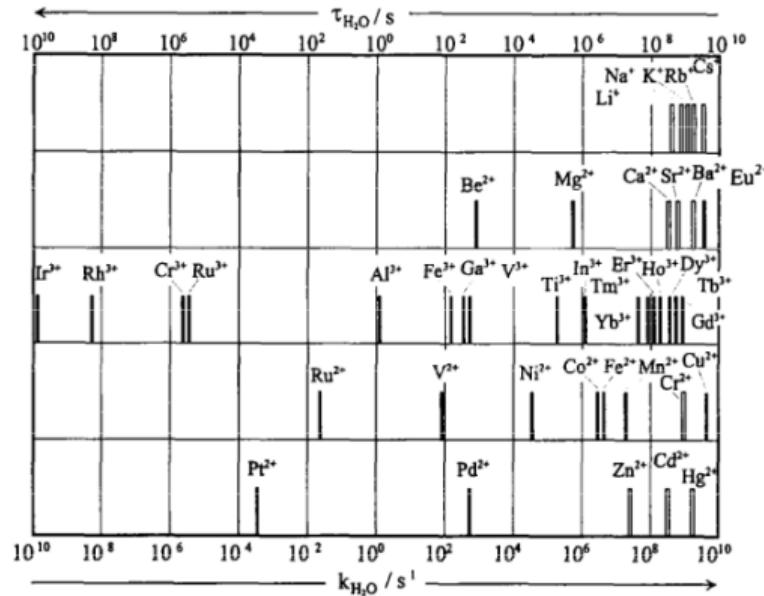
19.3.2025

Why?

-
- 1) L. Helm, et al. Water exchange on metal ions: experiments and simulations. *Coordination Chemistry Reviews*. 1999
 - 2) K. L. Milton, et al. Difference in Structure and Electronic Properties of Oxygen Vacancies in α -Quartz and α -Cristobalite Phases of SiO₂. *Materials*. 2023

Why?

1) Lifetime of water in the solvation layer

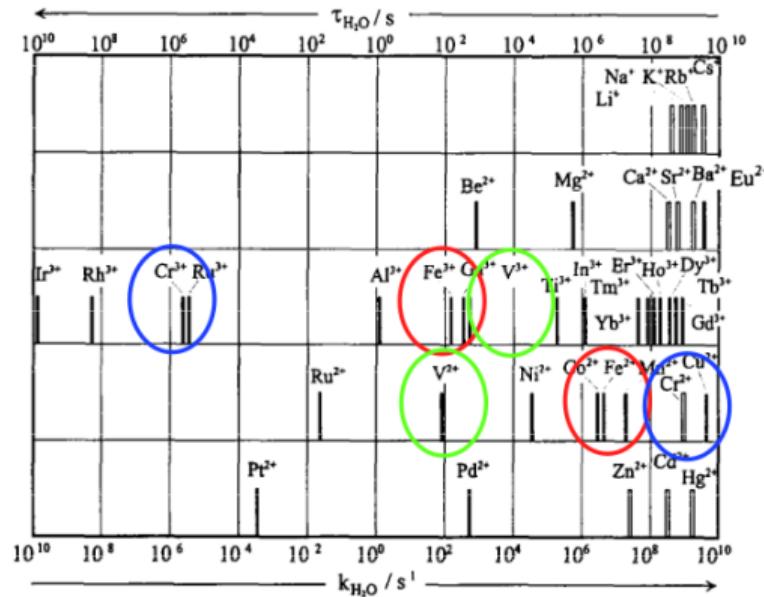


1) L. Helm, et al. Water exchange on metal ions: experiments and simulations. *Coordination Chemistry Reviews*. 1999

2) K. L. Milton, et al. Difference in Structure and Electronic Properties of Oxygen Vacancies in α -Quartz and α -Cristobalite Phases of SiO_2 . *Materials*. 2023

Why?

1) Lifetime of water in the solvation layer

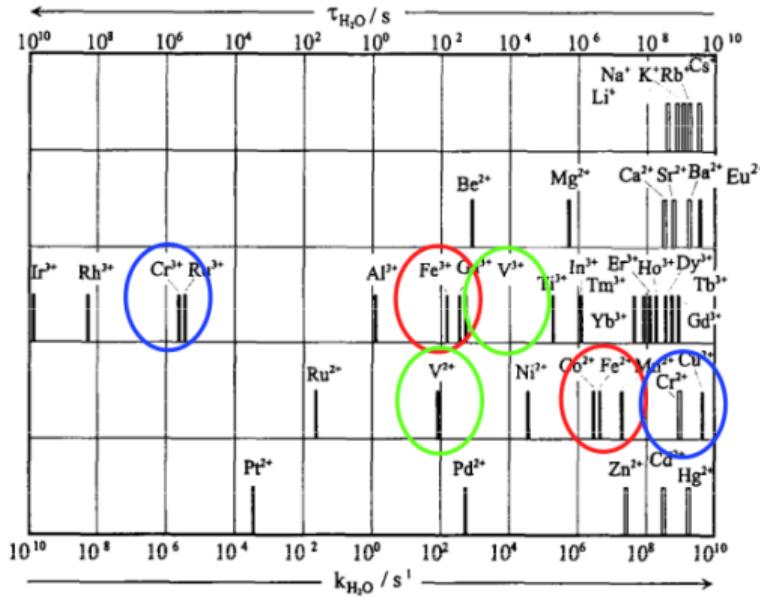


1) L. Helm, et al. Water exchange on metal ions: experiments and simulations. *Coordination Chemistry Reviews*. 1999

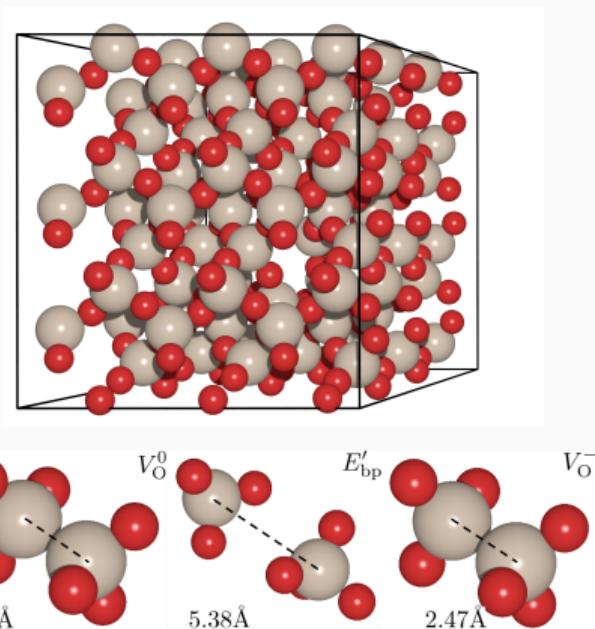
2) K. L. Milton, et al. Difference in Structure and Electronic Properties of Oxygen Vacancies in α -Quartz and α -Cristobalite Phases of SiO_2 . *Materials*. 2023

Why?

1) Lifetime of water in the solvation layer



2) Charge defects in SiO_2



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

2) K. L. Milton, et al. Difference in Structure and Electronic Properties of Oxygen Vacancies in α -Quartz and α -Cristobalite Phases of SiO_2 . *Materials*. 2023

Charge Equilibration

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

Charge Equilibration

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

χ - electronegativity

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

Charge Equilibration

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

χ - electronegativity

$$\min_{\mathbf{q}} E_{\text{QEeq}}, \sum_i q_i = Q_{\text{tot}}$$

1) **Closed form**

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

2) **Iteratively minimize with gradient descent**

QE Eq External Field

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

$$\min_{\mathbf{q}} E_{\text{QE Eq}}, \quad \sum_i q_i = Q_{\text{tot}}$$

1) Closed form

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

2) Iteratively minimize with gradient descent

QE_q in Machine Learning

Instead of **element**-dependent $\chi(\mu)$, ML-QE_q introduces **environment**-dependent $\chi(r)$

Gaussian Process Regression

- Local ML - GAP
- QE_q - kQE_q

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

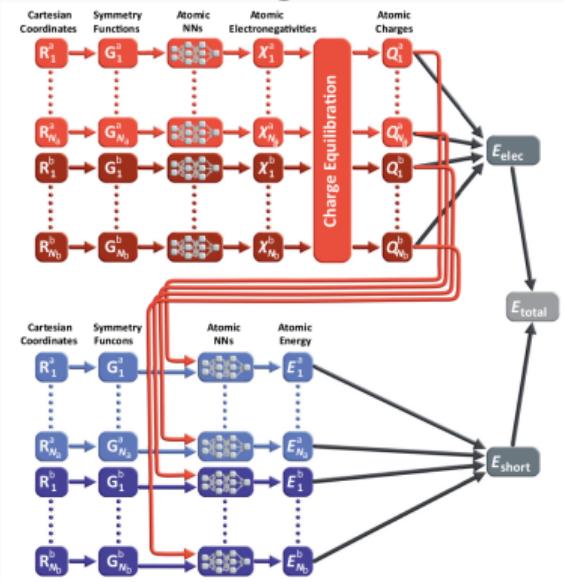
QE_q in Machine Learning

Gaussian Process Regression

- Local ML - GAP
- QE_q - kQE_q

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

4th Generation High-Dimensional NN



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

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

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

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

Gaussian Process Regression

- Local ML - GAP
- QE_q - kQE_q

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

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_q in Machine Learning

Gaussian Process Regression

- Local ML - GAP
- QE_q - kQE_q

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

Charge Constraint ACE

- PACE
- Equivariant

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

4th Generation High-Dimensional NN

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

MACE-QE_q

- Equivariant Message Passing NN

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

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

QE_q in Machine Learning

Gaussian Process Regression

- Local ML - GAP
- QE_q - kQE_q

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

Charge Constraint ACE

- PACE
- Equivariant

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

4th Generation High-Dimensional NN

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

MACE-QE_q

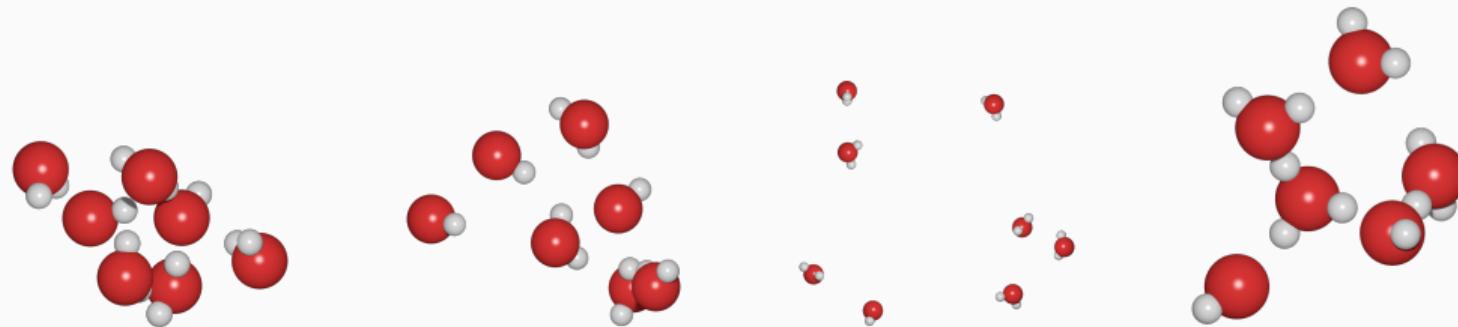
- Equivariant Message Passing NN

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

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

Water Clusters Dataset

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



Gaussian Process Regression

- 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_q:

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

Gaussian Process Regression

- 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_q:

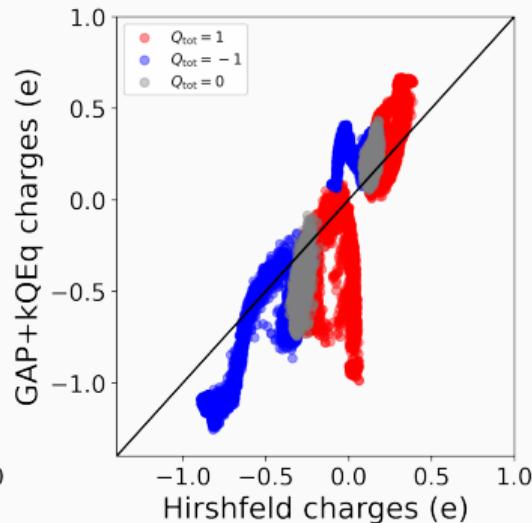
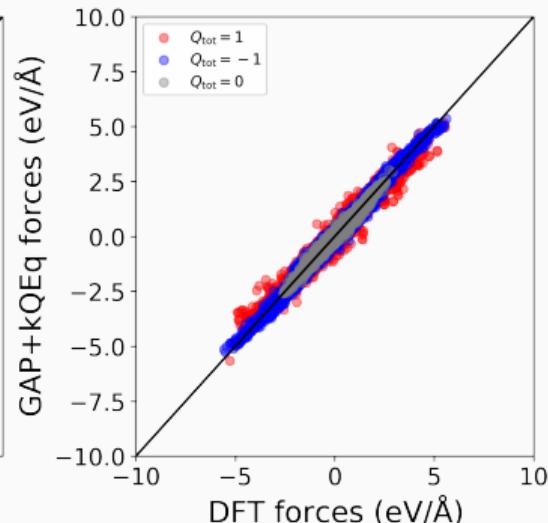
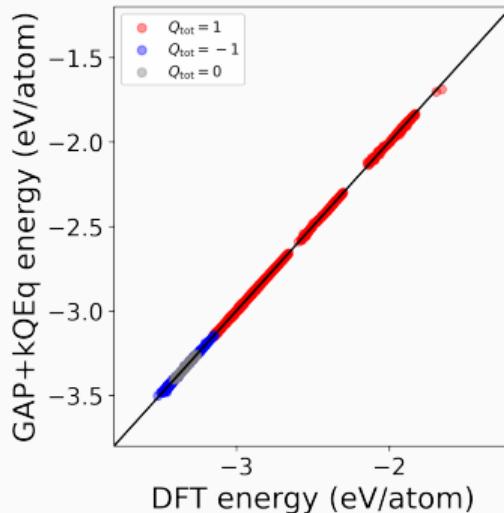
$$\chi(\mathbf{x}_i) = \sum_{m=1}^M w_m^{\text{kQE}_q} k(\mathbf{x}_i, \mathbf{x}_m)$$

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_q Water Clusters

- Water clusters (3-10 molecules)
- GAP + kQE_q model fitted on E , and F



MACE-QEq

- 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:

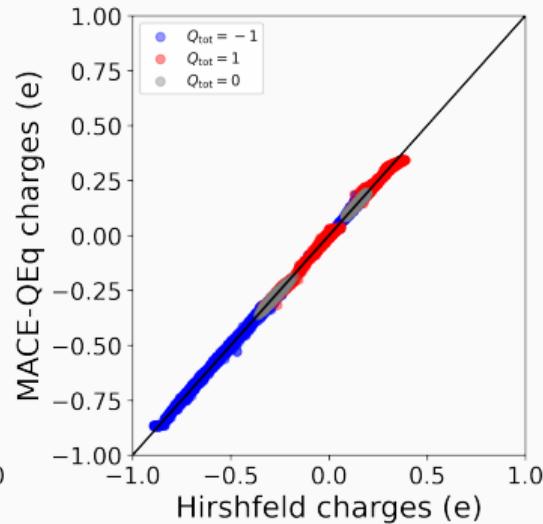
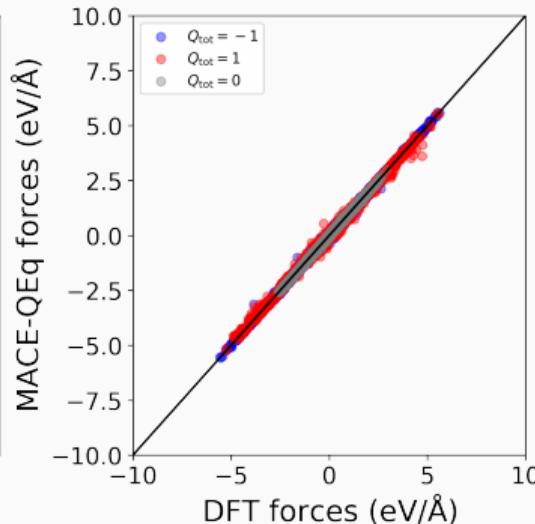
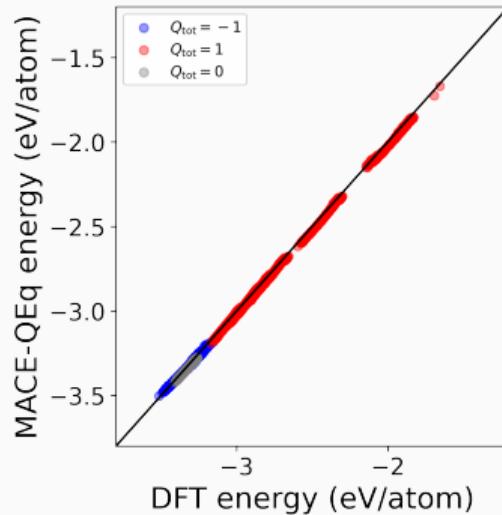
$$E_{\text{short}} = \sum_{i=0}^{N_{\text{at}}} \epsilon_i(\mathbf{h}_i) = \mathcal{R}_E^{(s)} \left(\mathbf{h}_i^{(s)} \right)$$

MACE-QEq electronegativities:

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

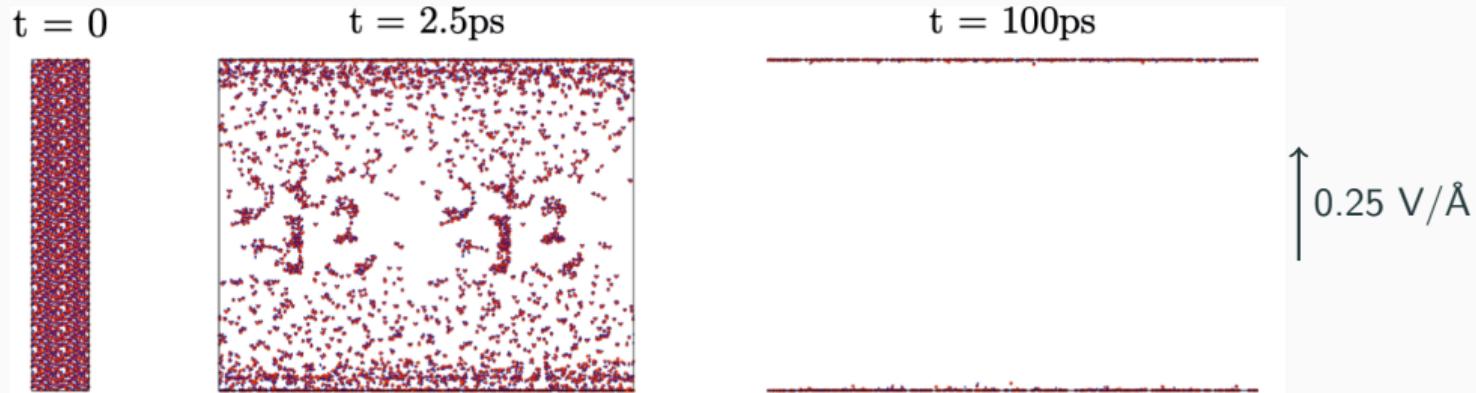
MACE-QEq Water Clusters

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

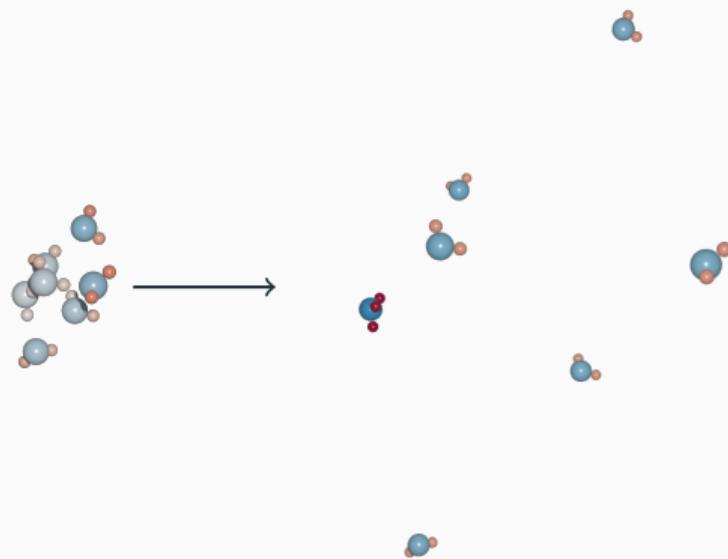


Limitations of QEq

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

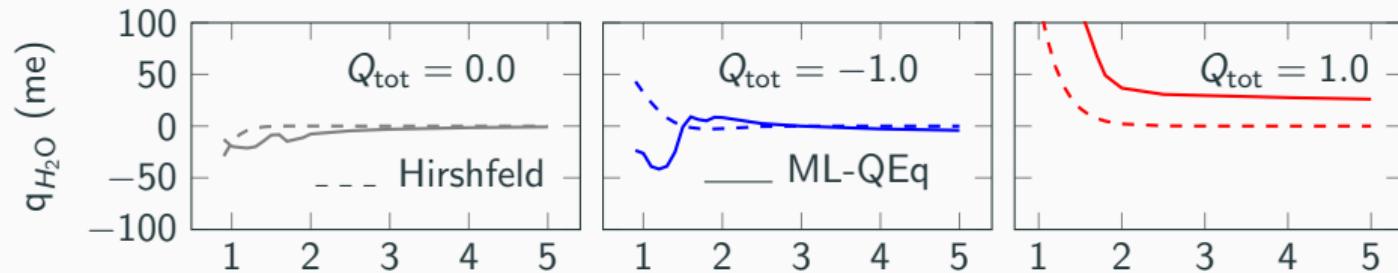


Charges of scaled water clusters

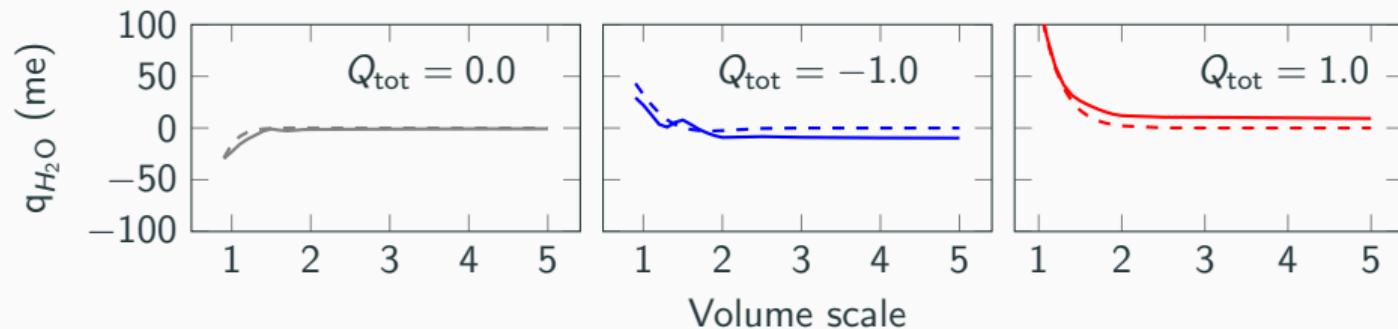


Charges of scaled water clusters

GAP + kQE_{Eq} model fitted to E and F

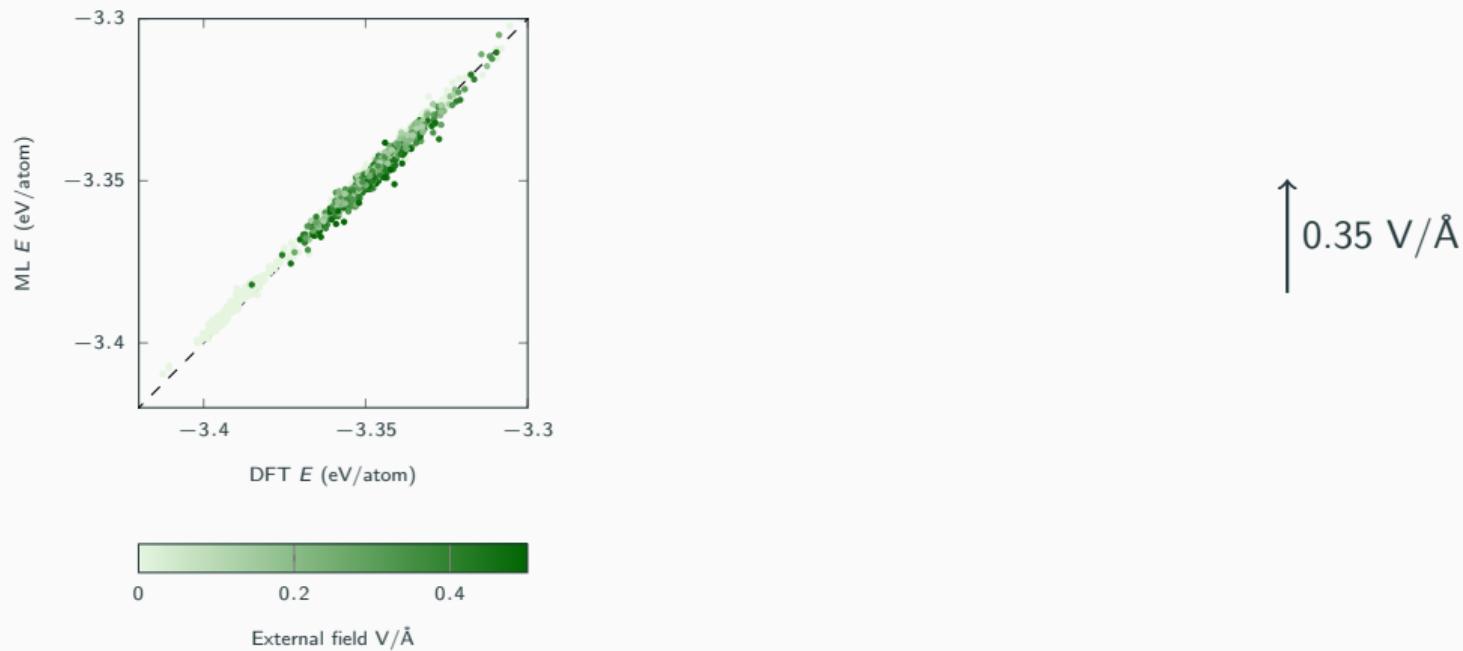


MACE-QEe model fitted to E , F , and q



ML-QEq External Field

- Neutral water molecules
- GAP+kQE_Q
- External fields $\epsilon \in (0.1, 0.5) \text{ V}/\text{\AA}$



QR codes!

GAP+kQE_q code



kQE_q paper



GAP+kQE_q paper

Almost done:

*Pushing Charge Equilibration
Based Machine Learning
Potentials to their Limits*

MACE-QE_q code and paper

Hopefully soon public



This presentation



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