Machine Learning the Electric Field Response of Condensed Phase Systems using Perturbed Neural Network Potentials

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Introduction I

- The interaction of condensed phase systems with external electric fields is a fundamental aspect of various natural and technological processes, including:
  - Biological processes: protein folding, cell signaling, and membrane transport
  - Energy storage and conversion: batteries, supercapacitors, and solar cells
  - Materials science: ferroelectricity, piezoelectricity, and electrostriction
- Understanding the behavior of condensed phase systems in the presence of electric fields is crucial for the development of new technologies and the optimization of existing ones.
- However, simulating these interactions using accurate methods like ab-initio molecular dynamics (AIMD) is computationally expensive and often limited to small system sizes and short timescales.

Introduction II

- Machine learning-based approaches offer a promising alternative for simulating the electric field response of condensed phase systems, enabling the study of larger systems and longer timescales.

Mathematical Background

- The Hamiltonian of a system in the presence of an external electric field can be written as:

$$H = H_0 + H_{\text{field}}$$

- The unperturbed Hamiltonian H_0 describes the system in the absence of the electric field.
- The field-dependent Hamiltonian H_{field} describes the interaction between the system and the electric field.

Mathematical Background (continued)

- $$H_E(\mathbf{r}^N, \mathbf{p}^N) = H_0(\mathbf{r}^N, \mathbf{p}^N) - \mathbf{E} \cdot \mathbf{M}(\mathbf{r}^N) \tag{1}$$

  where $H_0(\mathbf{r}^N, \mathbf{p}^N)$ is the total unperturbed Hamiltonian, comprised of the kinetic energy of the N nuclei with momenta $\mathbf{p}^N$ and the electronic potential energy depending on all nuclear positions $\mathbf{r}^N$, and $-\mathbf{E} \cdot \mathbf{M}(\mathbf{r}^N)$ is the perturbation induced by the electric field $\mathbf{E}$ acting on the total dipole moment of the system at zero field $\mathbf{M}(\mathbf{r}^N)$.

- $$F_{i\xi} = -\frac{\partial E_{\text{pot}}(\mathbf{r}^N)}{\partial r_{i\xi}} + \sum_{\zeta} \frac{\partial M_\zeta}{\partial r_{i\xi}} E_\zeta \tag{2}$$

  where $\zeta = x, y, z$ and $\xi = x, y, z$ represent the three Cartesian coordinates, and E_ζ is the ζ-component of the electric field $\mathbf{E}$.

Atomic Polar Tensor (APT)

- The APT is a tensor that describes the response of the system to the electric field.
- The first term is the force on the nuclei in the absence of an electric field, and the second term is the field-induced contribution which can be written in terms of the transpose of the Atomic Polar Tensor (APT) of atom i, $\mathbf{P}_i$.

$$\frac{\partial M_\zeta}{\partial r_{i\xi}} = \left[\mathbf{P}_i^T\right]_{\xi\zeta} \tag{3}$$

In this approach, they train two Machine Learning (ML) models, one for the potential energy ($E_{\text{pot}}(\mathbf{r}^N)$) and one for the APT ($\mathbf{P}_i$) and use the corresponding forces.

APT: Physical Interpretation

- The APT can be interpreted as a measure of the polarizability of the system.
- It describes how the dipole moment of the system changes in response to an external electric field.
- The APT is a tensor, which means that it has both magnitude and direction.

Perturbed Neural Network Potential Molecular Dynamics (PNNP MD)

- PNNP MD is a novel machine learning-based approach for simulating the electric field response of condensed phase systems.
- It combines the strengths of neural network potentials and perturbation theory to provide an accurate and efficient description of the electric field response.
- The key components of PNNP MD include:
  - A neural network potential that describes the unperturbed potential energy surface of the system.
  - A perturbation term that accounts for the interaction between the system and the electric field using atomic polar tensor (APT) that describes the response of the system to the electric field.

PNNP MD: Neural Network Potential (c-NNP)

- The neural network potential is trained on a dataset of configurations of the system in the absence of the electric field.
- The potential is represented as a sum of atomic contributions, each of which is a function of the positions of the atoms in the system.
- They use a committee of 2nd generation high-dimensional neural network potentials (c-NNP) to model $E_{pot}(r_N)$.

PNNP MD: Perturbation Term (APTNN)

- The perturbation term is derived from the interaction between the system and the electric field.
- It is represented as a sum of atomic contributions, each of which is a function of the positions of the atoms in the system and the electric field.
- They use an E(3)-equivariant graph neural network (APTNN) to model APT ($\mathbf{P}_i$)

c-NNP and APTNN Training Details

The committee members of the c-NNP were trained using n2p276. Parameters for the neural network were taken from a previous ML potential study on liquid water, in conjunction with generic symmetry functions.
c-NNP is trained on energies and forces obtained from DFT calculations at the level of RPBE-D3.

- c-NNP: Trained using active learning procedure reported in ref. 44
- APTNN: Trained using previously published model containing APTs from only 27 snapshots of an equilibrated 128 water molecule box in its training set at the level of RPBE-D337.

The resultant 10,368 APTs were obtained by single-point finite difference calculations.

Validation of PNNP: Force Prediction

- The PNNP method was validated by comparing the predicted forces with reference DFT forces.
- The results showed that the PNNP method is able to accurately predict the forces on water molecules.
- The root-mean-square-error (RMSE) of the PNNP forces was found to be around 90 meV $Å^{-1}$.

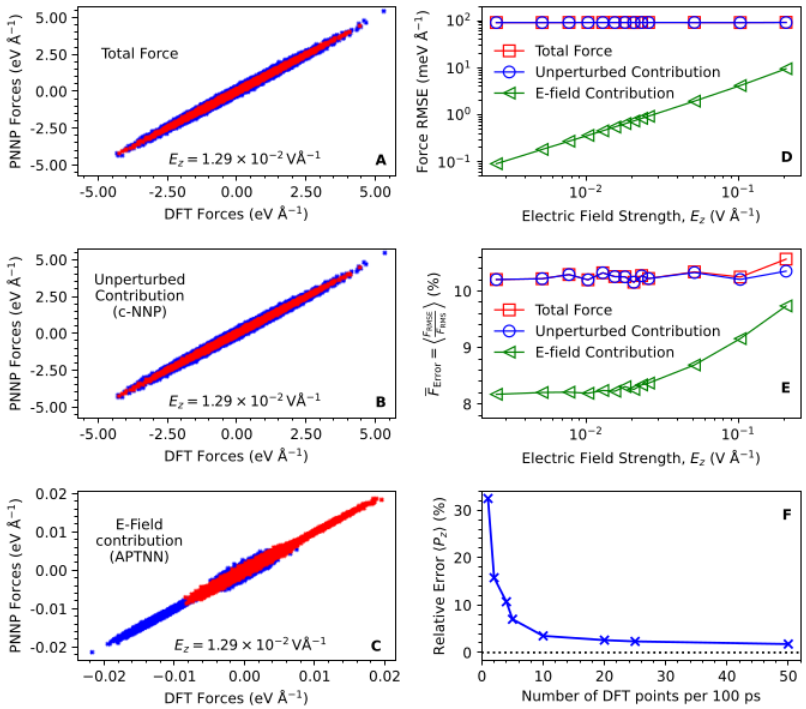

Fig. 1 | Error metrics of the trained Perturbed Neural Network Potential (PNNP). force, unperturbed force contribution and field-induced force contribut

Validation of PNNP: Force Prediction (continued)

- The PNNP method was able to accurately capture the unperturbed and field-induced force contributions.
- The RMSE of the field-induced force contribution was found to be around 8.6×10^{-2} meV Å^{-1} at 0.0026 V Å^{-1}.
- The results demonstrated the ability of the PNNP method to accurately predict the forces on water molecules under different electric field strengths.

Validation of PNNP: Orientational Relaxation Dynamics

- The orientational relaxation dynamics of water molecules in the presence of an electric field was studied using PNNP MD.
- The results were compared to those obtained from AIMD simulations.
- The PNNP MD results were found to be in excellent agreement with the AIMD results, demonstrating the accuracy of the PNNP method.

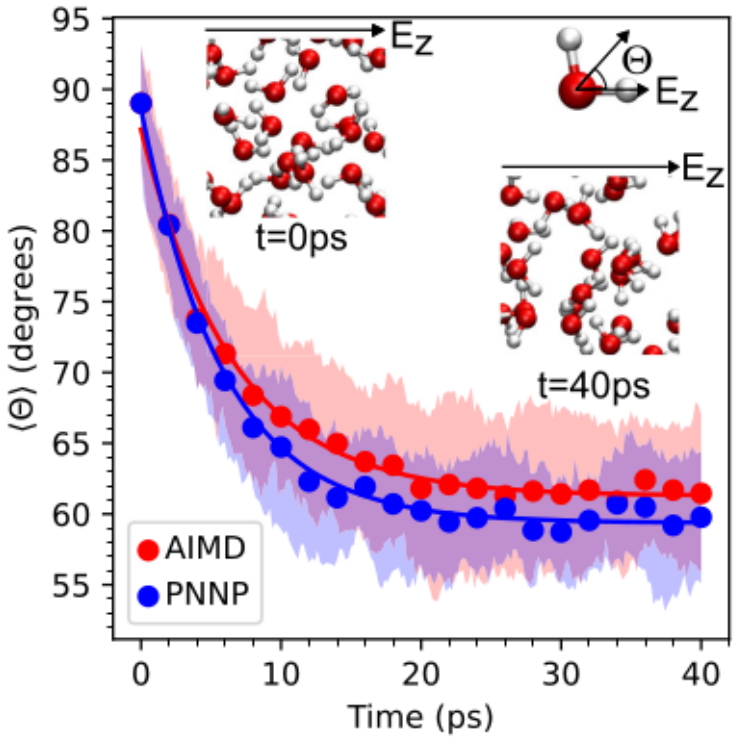

Fig. 2 | Electric field-induced orientational relaxation of liquid water.

Validation of PNNP: Orientational Relaxation Dynamics (continued)

- The orientational relaxation time was calculated from the PNNP MD simulations and compared to the AIMD results.
- The results showed that the PNNP MD method is able to accurately capture the orientational relaxation dynamics of water molecules in the presence of an electric field.

Validation of PNNP: Electric Field Sweep

- The electric field sweep was performed using PNNP MD to study the response of water molecules to different electric field strengths.
- The results were compared to those obtained from AIMD simulations.
- The PNNP MD results were found to be in excellent agreement with the AIMD results, demonstrating the accuracy of the PNNP method.

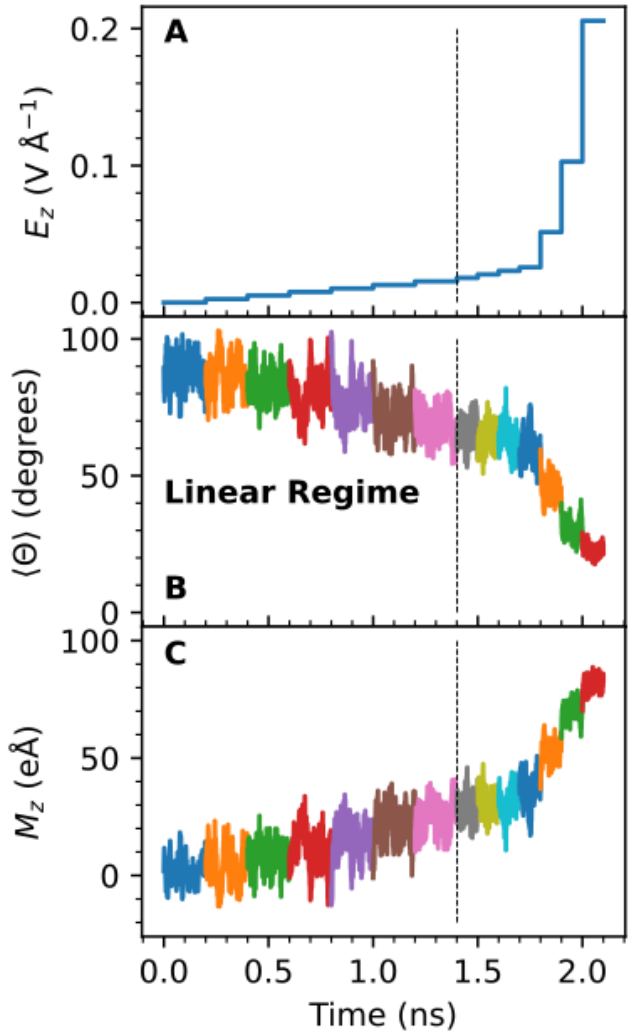

Fig. 3 | Electric field sweep for liquid water. The applied electric field alor

Validation of PNNP: Electric Field Sweep (continued)

- The electric field sweep results showed that the PNNP MD method is able to accurately capture the response of water molecules to different electric field strengths.
- The results also demonstrated the ability of the PNNP MD method to study the nonlinear response of water molecules to electric fields.

Dielectric Constant

- The dielectric constant of liquid water was calculated using the PNNP MD method.
- The results were obtained from the time-averaged polarization of liquid water as a function of the applied electric field.
- The dielectric constant was calculated using Eq. (7) and was found to be in agreement with the experimental value.

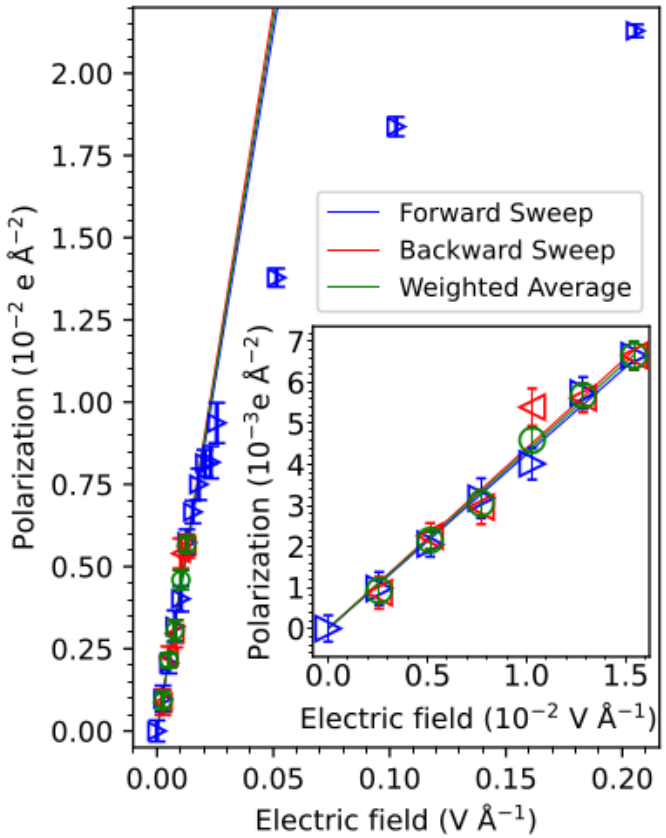

Fig. 4 | Polarization and dielectric constant. The time-averaged pola

Dielectric Constant (continued)

- The dielectric constant was converged after only about 175ps of simulation time per applied electric field.
- This is an order of magnitude less simulation time than what is required to calculate the dielectric constant from the fluctuations of the polarization.
- The results demonstrate the efficiency and accuracy of the PNNP MD method in calculating the dielectric constant of liquid water.

Comparison with Zero-Field Simulation

- The dielectric constant was also calculated from the fluctuations of the polarization at zero electric field using Eq. (8).
- The result was found to be different from the value obtained from the electric field sweep.
- The reason for the difference is not known, but could be due to simulation details or approximations made in deriving the dielectric constant.

Field-Dependent IR Spectrum of Liquid Water: Results

- The calculated IR spectrum at zero field strength agrees well with the experimental spectrum.
- The spectrum remains insensitive to the presence of an electric field up to about 0.0514 V $Å^{-1}$.
- In larger fields, OH stretch vibrations red-shift, indicating stronger intermolecular hydrogen bonding. Simultaneously, the librational band shifts to blue, suggesting a stiffer potential for water molecule rotations.

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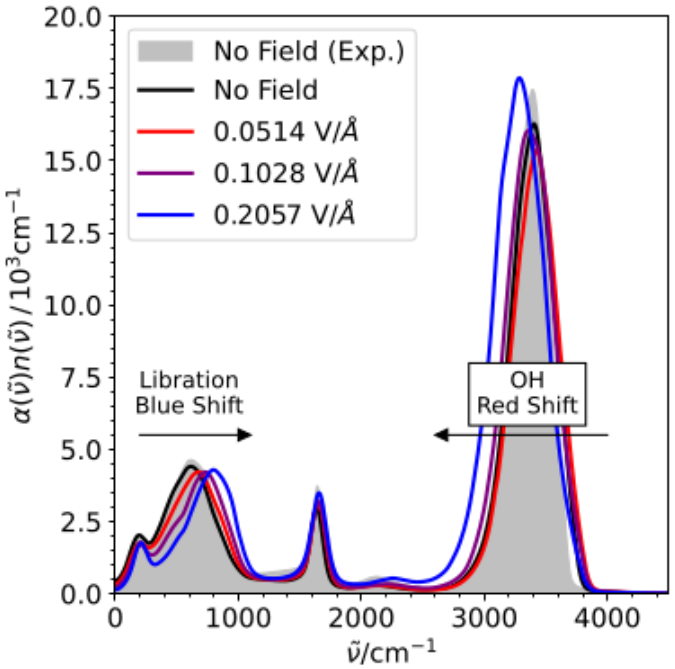

Fig. 5 | Field-dependent Infrared (IR) spectrum of liquid water. The p

Advantages of PNNP MD

- **High accuracy**: PNNP MD has been shown to be highly accurate in simulating the behavior of water molecules in the presence of electric fields.
- **Efficient**: PNNP MD is computationally efficient, allowing for simulations of large systems and long timescales.
- **Flexible**: PNNP MD can be used to simulate a wide range of systems, including molecules, solids, and liquids.
- **Transferable**: PNNP MD can be used to simulate systems with different electric field strengths and orientations.
- **Interpretable**: PNNP MD provides a clear and interpretable understanding of the behavior of water molecules in the presence of electric fields.

Advantages of PNNP MD (continued)

- **No need for explicit solvent**: PNNP MD does not require the explicit inclusion of solvent molecules, making it more efficient and scalable.
- **No need for periodic boundary conditions**: PNNP MD does not require periodic boundary conditions, making it more flexible and applicable to a wide range of systems.
- **Can be used with different force fields**: PNNP MD can be used with different force fields, making it more versatile and adaptable.

Disadvantages of PNNP MD

- **Requires training data**: PNNP MD requires a large amount of training data to learn the behavior of water molecules in the presence of electric fields.
- **May not be accurate for all systems**: PNNP MD may not be accurate for all systems, particularly those with complex or unusual behavior.
- **May require careful parameterization**: PNNP MD may require careful parameterization to achieve accurate results.
- **May be computationally expensive for large systems**: PNNP MD may be computationally expensive for large systems, particularly those with many atoms or complex geometries.

Disadvantages of PNNP MD (continued)

- **May require additional corrections**: PNNP MD may require additional corrections or modifications to achieve accurate results.
- **May be sensitive to initial conditions**: PNNP MD may be sensitive to initial conditions, particularly for systems with complex or chaotic behavior.

Conclusion

- PNNP MD is a powerful tool for simulating the behavior of water molecules in the presence of electric fields.
- The method has been shown to be highly accurate and efficient, making it an attractive alternative to traditional simulation methods.
- PNNP MD has the potential to be used in a wide range of applications, including the study of biological systems, materials science, and energy storage and conversion.

Conclusion (continued)

- The results of this study demonstrate the potential of PNNP MD to simulate the behavior of water molecules in the presence of electric fields.
- The method has been shown to be highly accurate and efficient, making it an attractive alternative to traditional simulation methods.
- Future studies will focus on applying PNNP MD to a wide range of systems, including biological systems, materials science, and energy storage and conversion.

Future Work

- Future studies will focus on applying PNNP MD to a wide range of systems, including biological systems, materials science, and energy storage and conversion.
- The method will be used to study the behavior of water molecules in the presence of electric fields, as well as other systems such as ions, molecules, and solids.
- The results of these studies will provide a deeper understanding of the behavior of these systems and will have important implications for a wide range of fields.

Future Work (continued)

- Future studies will also focus on developing new methods and techniques for simulating the behavior of water molecules in the presence of electric fields.
- These methods will include the development of new force fields, as well as the use of machine learning and other advanced simulation techniques.
- The results of these studies will provide a deeper understanding of the behavior of water molecules in the presence of electric fields and will have important implications for a wide range of fields.