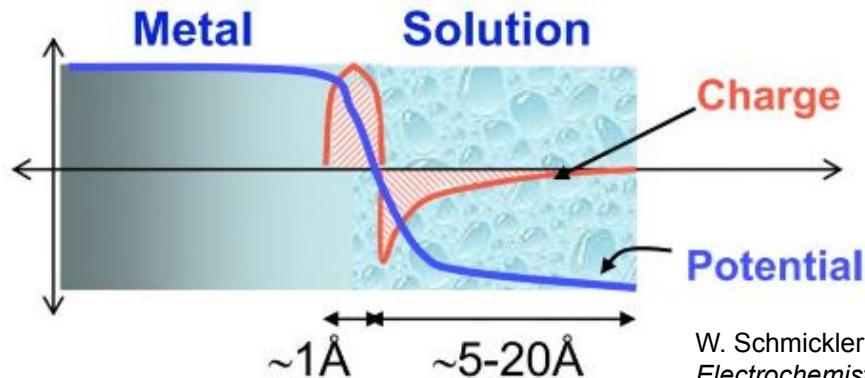


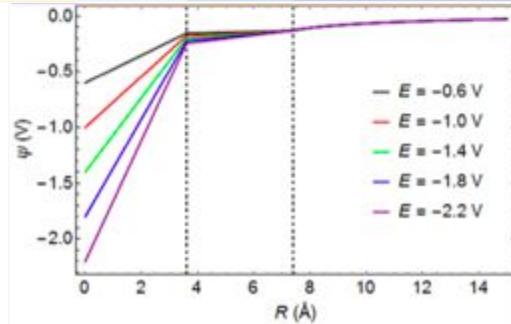
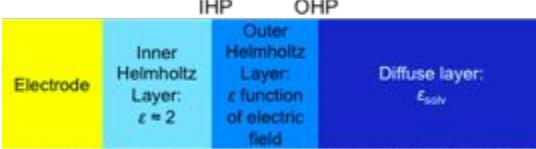
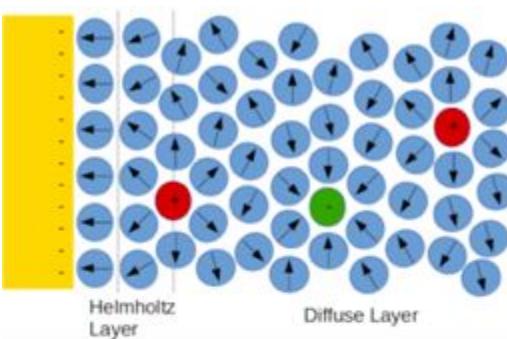
# A practical introduction to applied electrode potentials in atomistic simulation

Zachary K. Goldsmith  
CCCE Electronic Structure meeting  
April 25<sup>th</sup>, 2025

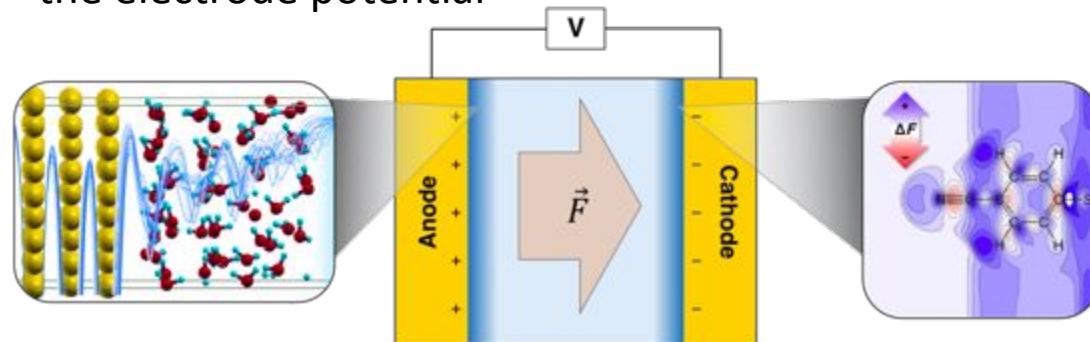


W. Schmickler & E. Santos, *Interfacial Electrochemistry*, 2010

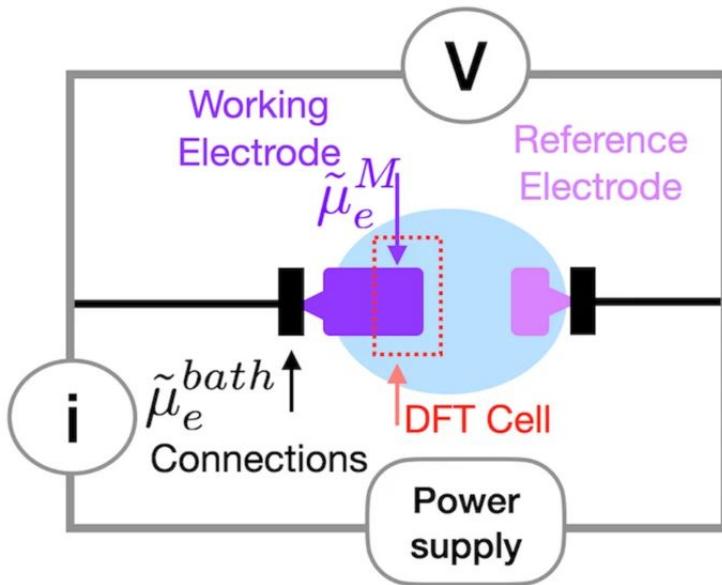
# Atomistic modeling of electrochemical interfaces



- Electrode-electrolyte interfaces are uniquely challenging for accurate, atomistic simulation
- Application of electrode potential may require working in the grand-canonical ensemble with respect to  $N_e$
- Response of polar solvent molecules and electrolyte ions forms the electrical double layer (EDL) which has unique, anisotropic properties
- This talk will focus on properly applying and discerning the electrode potential



# The electrode potential



Melander, Wu, Weckman, Honkala,  
*npj Comput. Mat.*, 2024

- Cell voltage is governed by the voltage difference between the anode and cathode
  - Experimentally this is often done against a reference electrode
- Electrons freely flow through the circuitry to maintain this voltage
- Periodic DFT cell can only realistically accommodate a half-cell: one electrode and its interface with electrolyte
- How can one apply and control an electrode potential that is necessarily defined relative to a counter electrode?

NB: batteries are Galvanic—not electrolytic—cells so there isn't an external power supply

# The electrode potential has several expressions

## THE “ABSOLUTE” ELECTRODE POTENTIAL—THE END OF THE STORY

SERGIO TRASATTI

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Milan, Italy

(Received 13 February 1989)

*Electrochim. Acta*

**Abstract**—A unifying derivation of the various concepts of “absolute” electrode potential is provided starting from a simple electrochemical cell. The approach proves that all kinds of “absolute” potential are implicit in the thermodynamics of the cell and all have the same conceptual validity. Therefore, the relevant question is not which is the true “absolute” electrode potential, but which provides the most convenient reference for a practical impact.

Comparison with Equation (2) shows that

$$_2E_a^M = (\phi^M - \phi^S) - \mu_e^M, \quad (14)$$

also fulfills the requirements to be termed “absolute” electrode potential. It is straightforward that  $_2E_a^M$  implies the inner (Galvani) electric potential of the solution as the reference state. This is the potential

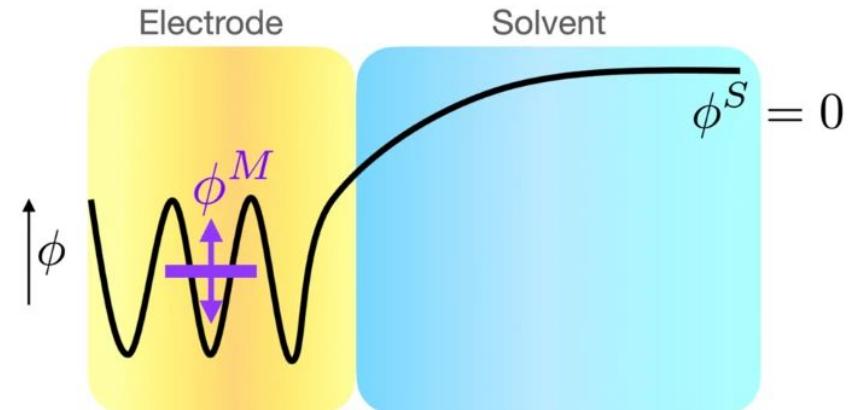
- Trasatti unified existing definitions using the rigorous thermochemical origins of electrode potentials
- Defined electrode potentials using computationally realizable terms, i.e. electrostatic (Hartree) potential values and chemical potentials of electrons (Fermi energy)

# Expressing electrode potential in a half-cell

is not the only available option. There are at least four different single potential definitions<sup>3</sup> each with different scales and reference systems, but all of them can be presented formally using the reduced absolute potential<sup>3,44</sup>

$$U^M(\text{abs}) = \Delta_S^M \phi - \mu_e^M + K \quad (2)$$

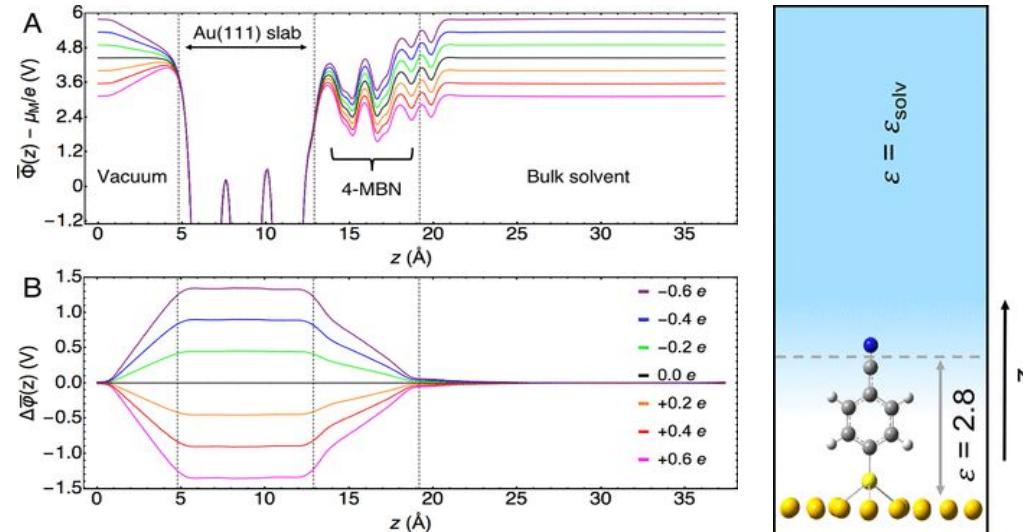
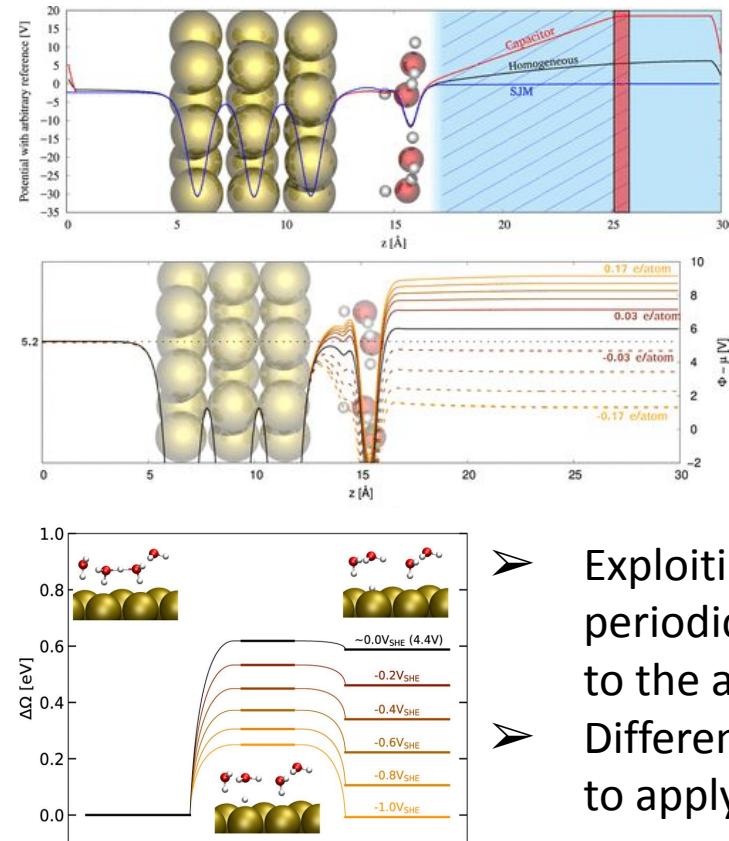
where  $\mu_e^M$  is an intrinsic material property and independent of the electrode potential.  $\Delta_S^M \phi = \phi^M - \phi^S$  stands for the inner potential difference, i.e. the electrostatic potential difference between the bulk of electrode (M) and solution (S) as shown in Fig. 2.  $K$  is a constant and depends on the chosen scale, which in DFT simulations is typically chosen<sup>6</sup> as the electrostatic potential in vacuum or the inner potential of the implicit solvent, in which case  $U_{\text{vac}}^M(\text{abs}) = -\tilde{\mu}_e^M = -E_F^{\text{DFT}}$ <sup>3,45</sup>.



- Absolute potential can be expressed in terms of the electrostatic potential difference between deep in the metal and deep in solution as well as the intrinsic chemical potential of electrons in the metal (Fermi energy or inverse work function)
- How does this work practically?

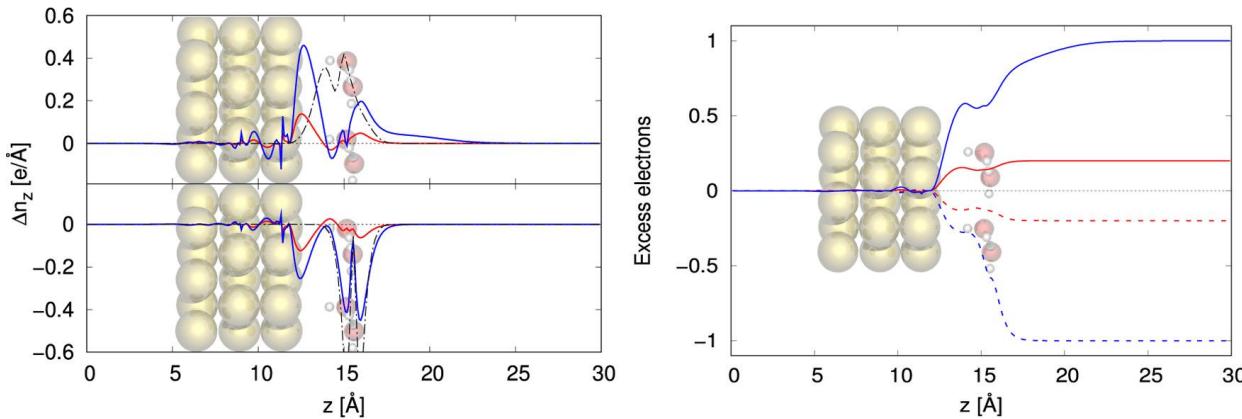
NB:  $\phi^S = 0$  is a boundary condition that emerges from EDL theory

# Electrode potential in practice: Static calculations



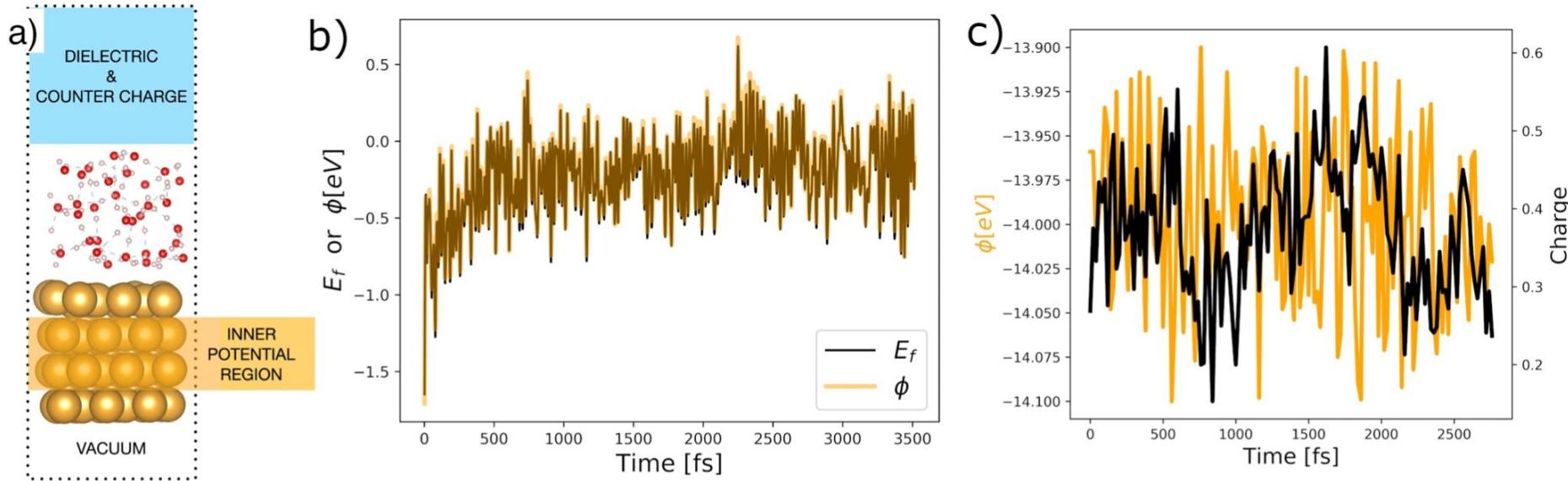
- Exploiting fractional charge and implicit solvation in periodic DFT calculations allows for smooth change to the applied voltage
- Differential capacitance governs the charge needed to apply a given potential

# Electrode potential in practice



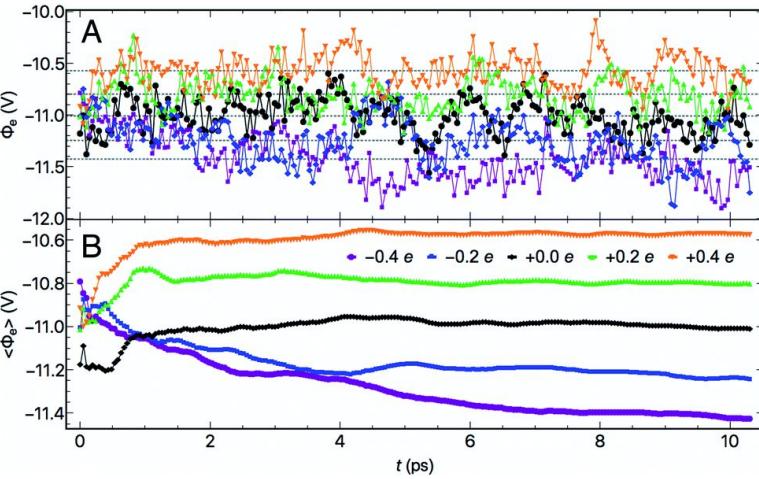
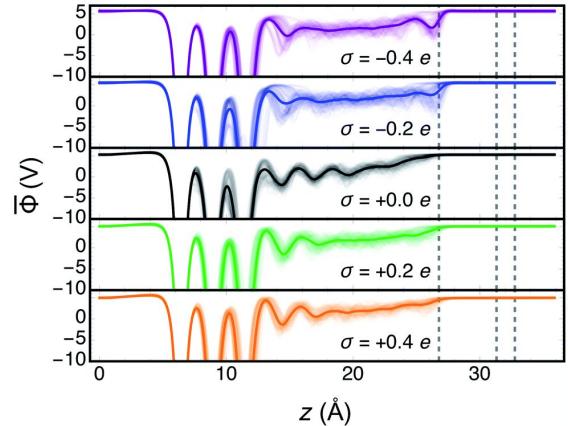
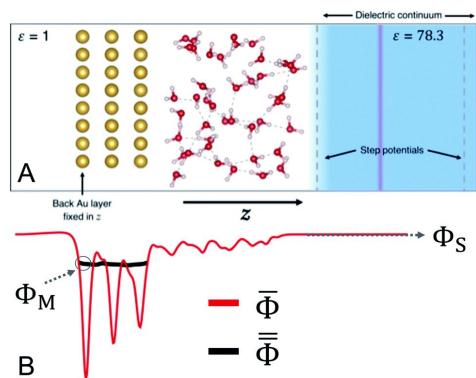
- Note that a carefully constructed and bounded simulation cell allows for overwhelming localization of excess charge on one “active” surface

# Dynamics exhibit the charge-potential relationship

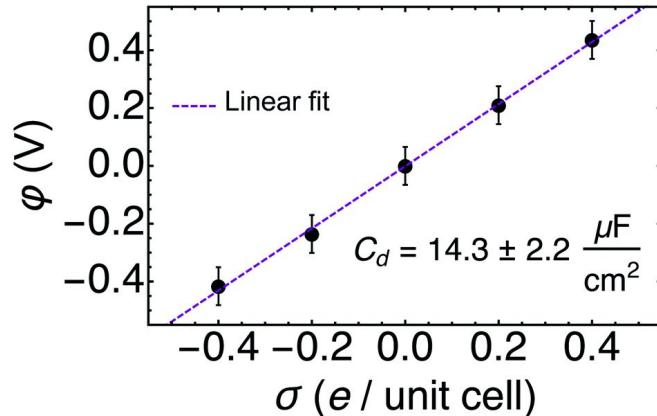


- AIMD of water @ negatively polarized gold electrode done with both fixed charge and fixed (inner) potential
- Charge and potential behave like conjugate variables: fix one and the other fluctuates around an equilibrium value

# Dynamics exhibit the charge-potential relationship

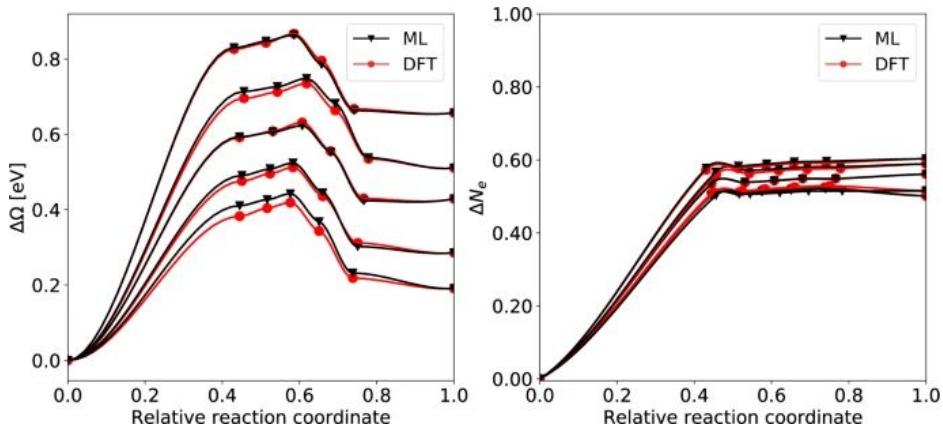
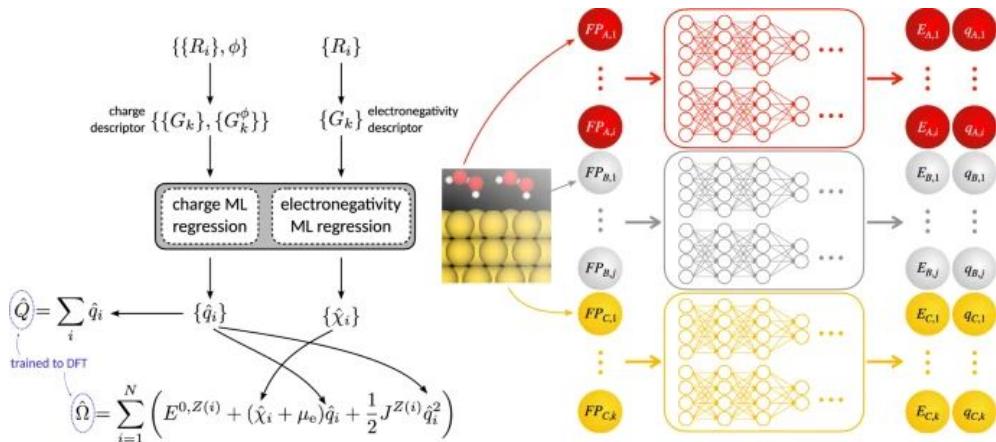


- AIMD of water @ gold electrode w/ 5 different constant charge values
- Average potential converges despite significant, persistent fluctuations
- Differential capacitance in agreement with experiment



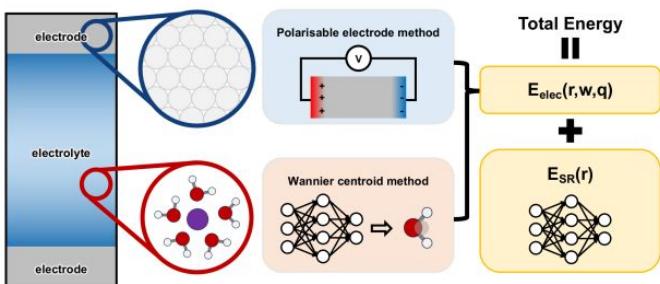
# Looking ahead: Applied potential in (MLFF)MD

- Machine-learning in the GC ensemble for proton discharge on gold with QRNN/MPNICE-like approach
  - Auxiliary NNs predict charges and electronegativities at a given applied voltage



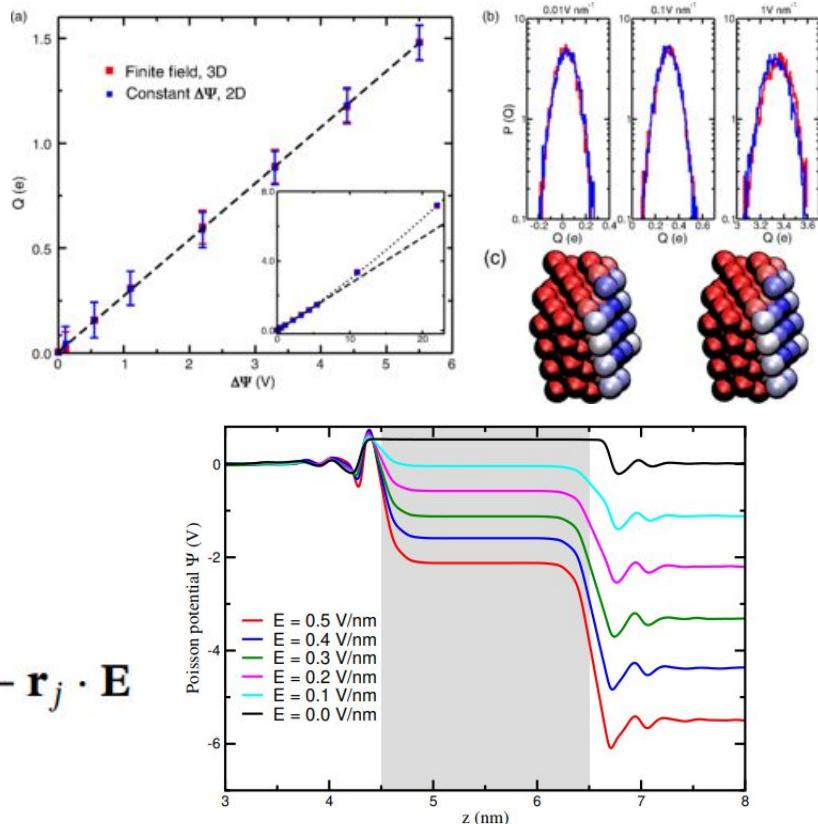
# Looking ahead: Applied potential in (MLFF)MD

- In FF simulations fractional charge and its localization can't be easily controlled
- However, we recover the ability to simulate both electrode poles
- This avails coupling an external electric field to the charge model of the FF
  - Valid only in linear response regime, but this is likely a good approximation
  - How straightforward this will be for ab initio-quality MLFFs is yet to be seen



$$\Psi_j = \Psi_j^{\text{PBC}} - \mathbf{r}_j \cdot \mathbf{E}$$

Zhu & Cheng, arXiv, 2024



Dufils et al., PRL, 2019