Unified Approach to Implicit and Explicit Solvent Simulations of Electrochemical Reaction Energetics

Joseph Gauthier, Colin Dickens, Hendrik H. Heenen, Stefan Ringe, Karen Chan

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One of the major open challenges in ab initio simulations of the electrochemical interface is the determination of electrochemical barriers under a constant driving force. Existing methods to do so include extrapolation techniques based on fully explicit treatments of the electrolyte, as well as implicit solvent models which allow for a continuous variation in electrolyte charge. Emerging hybrid continuum models have the potential to revolutionize the field, since they account for the electrolyte with little computational cost while retaining some explicit electrolyte, representing a “best of both worlds” method. In this work, we present a unified approach to determine reaction energetics from both fully explicit, implicit, and hybrid treatments of the electrolyte based on a new multi-capacitor model of the electrochemical interface. A given electrode potential can be achieved by a variety of interfacial structures; a crucial insight from this work is that the effective surface charge gives the true driving force of electrochemical processes. In contrast, we show that the traditionally considered work function gives rise to multi-valued functions depending on the simulation cell size. Furthermore, we show that the reaction energetics are largely insensitive to the countercharge distribution chosen in hybrid implicit/explicit models, which means that any of the myriad implicit electrolyte models can be equivalently applied. This work thus paves the way for the accurate treatment of ab initio reaction energetics of general surface electrochemical processes using both implicit and explicit electrolyte.

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Unified approach to implicit and explicit solvent simulations of electrochemical reaction energetics

Joseph A. Gauthier,^{†,‡} Colin F. Dickens,^{†,‡} Hendrik H. Heenen,[¶] Stefan Ringe,^{‡,†}
and Karen Chan*,[¶]

[†]*SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States*

[‡]*SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, United States*

[¶]*Department of Physics, Technical University of Denmark, DK-2800, Kgs. Lyngby, Denmark*

E-mail: kchan@fysik.dtu.dk

Abstract

One of the major open challenges in *ab initio* simulations of the electrochemical interface is the determination of electrochemical barriers under a constant driving force. Existing methods to do so include extrapolation techniques based on fully explicit treatments of the electrolyte, as well as implicit solvent models which allow for a continuous variation in electrolyte charge. Emerging hybrid continuum models have the potential to revolutionize the field, since they account for the electrolyte with little computational cost while retaining some explicit electrolyte, representing a “best of both worlds” method. In this work, we present a unified approach to determine reaction energetics from both fully explicit, implicit, and hybrid treatments of the electrolyte based on a new multi-capacitor model of the electrochemical interface. A

given electrode potential can be achieved by a variety of interfacial structures; a crucial insight from this work is that the *effective* surface charge gives the true driving force of electrochemical processes. In contrast, we show that the traditionally considered work function gives rise to multi-valued functions depending on the simulation cell size. Furthermore, we show that the reaction energetics are largely insensitive to the countercharge distribution chosen in hybrid implicit/explicit models, which means that any of the myriad implicit electrolyte models can be equivalently applied. This work thus paves the way for the accurate treatment of *ab initio* reaction energetics of general surface electrochemical processes using both implicit and explicit electrolyte.

Introduction

Computational chemistry tools developed over the past several decades have allowed for an unprecedented level of mechanistic understanding in a wide variety of interface phenomena.^{1–22} In particular, electrocatalysis has experienced a rapid expansion with the application of density functional theory (DFT). The computational hydrogen electrode model²³ has, in the past 15 years, enabled the determination of the thermochemistry of coupled ion-electron transfers using simple surface science calculations. For a number of applications, however, electrochemical reaction barriers,^{24–37} electric field,^{38–40} and pH effects,^{41–43} are important, and all these elements require careful consideration of the electrolyte. Several methods have since been developed to model the electrochemical interface in *ab initio* simulations. Fully explicit simulations of the electrolyte^{44–46} have been developed, and in parallel, different implicit solvation methods have been implemented in a variety of commonly used DFT codes.^{17,47–64}

Each of these techniques comes with their own advantages and shortcomings. Fully explicit techniques give atomistic insight to the effects of solvation and the effect of electric field on reaction energetics.^{13,40,44} However, they frequently rely on expensive electrolyte sampling methods,^{11,65–67} and furthermore suffer from issues related to band misalignment,⁶⁸ stem-

ming from the well known failure of GGA-DFT under-predicting bandgaps.⁶⁹ Continuum methods present thermodynamic averages of solvation and therefore do not rely on expensive sampling techniques. They do however come with a variety of challenges⁷⁰ primarily from the marrying of the classical treatment of solvation with the atomistic treatment of the surface. Most importantly, continuum methods intrinsically cannot reproduce the chemical interaction of the surface with ions, since the charge is necessarily smeared over the entire electrode surface. Solvation energies for these methods have primarily been fit to molecular solutes, since that is the source of most experimental reference data.^{47,54,56,71} Little work has been done to benchmark these energies on extended surfaces, where hydrogen bonding has been shown to be important.^{25,72-74} For these reasons, hybrid approaches, including both some explicit electrolyte molecules and continuum solvation, are receiving a growing amount of attention.^{75,76}

Figure 1: Schematic of three current state of the art methods for calculating reaction energetics at constant driving force. (a) Schematic of cell extrapolation for two cell sizes, and illustration of charge partitioning (e.g. Bader) to determine the charge of the ion at the interface for charge extrapolation. (b) Charge extrapolation technique, with charges determined by partitioning as illustrated in (a). (c) Continuum charging, which exchanges electrons with an external reservoir to achieve constant work function. Counter charge is placed in the electrolyte to retain overall charge neutrality.

Real electrochemical systems operate at a constant applied electrode potential, and so there has been an effort to develop computational models that allow for simulations at constant potential. This is particularly challenging, since the work function, which defines the potential in *ab initio* simulations, changes across the reaction coordinate due to the use of finite simulation cell sizes. Figure 1 illustrates three classes of techniques used currently to solve the problem of changing work function across the reaction coordinate during charge transfer reaction events. Cell extrapolation, illustrated in Figure 1(a), relies on systematically increasing the size of the simulation cell in order to more closely approximate the infinite cell size limit. This approach can be quite expensive computationally, owing to the roughly cubic scaling of DFT with system size.⁷⁷ Charge extrapolation, illustrated in Figure 1(b), instead utilizes a mean-field (i.e. capacitor) approximation of the interface to predict the slope of the energy as a function of potential, which is proportional to the change in charge between states. The primary difficulty with this method is identifying the charge in each state. Previous work has shown that the charge resulting from charge partitioning schemes (e.g. Bader⁷⁸⁻⁸⁰) can accurately reproduce the results from cell extrapolation,^{45,46} but it is not clear how to partition charge for field-sensitive chemical steps. Finally, continuum charging methods, shown in Figure 1(c), allows for continuous variation in charge, leading to the possibility of the work function being constant between states at little additional computational cost.⁷⁵

In the present work, we present a unified approach to determining reaction energetics for general hybrid or fully explicit electrolyte models of the interface. This framework is based on 1) a *multi-capacitor* model of the various components of an electrochemical interface in atomistic DFT simulations 2) the idea that an *effective surface charge density* is the appropriate descriptor for the electrochemical driving force of electrochemical reactions, as opposed to the generally applied work function. The latter is essentially a reformulation of the Frumkin correction to reaction kinetics,^{81,82} which emphasizes that the *local* potential drop at the interface between the metal and reaction plane potential is the driving force

for electrochemical reactions. What we assert here is that this local potential drop is best approximated by an *effective* surface charge density. In contrast, the traditional use of work function as a descriptor of the driving force leads to multi-valued, cell-size dependent functions of reaction energetics in hybrid implicit/explicit simulations. We further show that, within our framework, the reaction energetics are essentially insensitive to the distribution of the continuum countercharge, which means that any of the myriad of existing implicit electrolyte models can be equivalently applied. By using the effective surface charge as the descriptor for the driving force, we importantly avoid the need to parameterize the continuum model to accurately predict capacitances, for which experimental data can be lacking. The capacitances also vary significantly upon the addition of explicit water layer(s) or at significant coverages of certain adsorbates, which renders parametrizations to bare surfaces obsolete. The energetics obtained through our method as a function of surface charge can be related to experimental activities through a coupled double-layer charging kinetic model, where diffuse layer effects can be accounted for. The framework we present here solves the observed cell-size dependence in hybrid explicit-implicit solvation constant potential simulations, and therefore represents a major step forward in the computational modeling of electrochemical reaction energetics.

Theoretical Methods and Models

This work uses the Vienna ab-initio Software Package^{83–85} in conjunction with VASPsol,^{56,57} as well as QUANTUM-ESPRESSO⁸⁶ (QE) in conjunction with the Environ⁴⁷ solvation module. Using VASP, core electrons were modeled with projector augmented wave pseudopotentials; using QE, core electrons were modeled using GBRV ultrasoft pseudopotentials.⁸⁷ In both DFT codes, valence electrons were expanded as plane-waves up to a kinetic energy cutoff of 500 eV. Exchange and correlation interactions were accounted for using the RPBE functional⁸⁸ in both codes. When optimizing bulk platinum to determine the appropriate

lattice constant, the Brillouin zone was sampled with a 12 x 12 x 12 γ -centered Monkhorst-Pack⁸⁹ k-point mesh. The optimized Pt lattice constant was determined to be 3.990 Å in VASP, and the optimized Cu lattice constant was found to be 3.6 Å in QE.

Geometries were considered optimized when the maximum force on any unconstrained atom in the system was below 0.03 eV Å⁻¹. For each electronic self-consistent field calculation, the density was considered to have converged when the total energy changed by less than 10⁻⁴ eV between steps. Separation between periodic images was set to be 8 Å. Using our previously published methodology,⁹⁰ we have corrected the constant charge reaction energetics by $q\Delta\Phi_{\text{vac}}$, where q is the (implicit) system charge and Φ_{vac} is the potential of the electrolyte region. This accounts for the shift in potential necessary with VASPsol and eliminates cell height dependence of the energetics. To avoid possible spurious dipole interactions, our simulation cells are symmetric along the direction normal to the surface.

VASPsol and Environ both treat the electrolyte at the electrochemical interface as a polarizable continuum. VASPsol places counter-charge via the linearized Poisson-Boltzmann equation, while Environ allows for a variety of countercharge placement models. In this work, except when stated otherwise, we use VASPsol, which places countercharge by solving the linearized Poisson-Boltzmann equation. Within this model we choose a Debye length of 3.0 Å, corresponding to a bulk ion concentration of 1.0 M. We set the effective surface tension to zero to avoid numerical instabilities, as reported in a recent perspective.⁷⁰ When Environ is used, we use the planar countercharge, modified Poisson-Boltzmann, and linearized modified Poisson-Boltzmann countercharge placement models. We use the standard g03-SCCS solvation parameters.⁴⁷ Details regarding the implementation of these solvation models can be found in their documentation.^{47,56,57}

Results and Discussion

We consider different kinds of charged interfacial systems as visualized in Figure 2: adsorbed partially negatively charged CO_2 , explicitly modeled hydronium cations and a continuum representation of electrolyte counter ions at the outer Helmholtz plane. All of these systems give rise to a separation of negative and positive charge, which can be effectively envisioned as local capacitors. In the case of explicit (e.g. proton) charge, the effective capacitor charge is just that of the proton itself, which is slightly less than unity.⁹¹ In the case of CO_2 , partial charge, corresponding to the electrosorption valency, is transferred during the adsorption process which leads to the creation of a strong dipole moment.^{92–94}

Figure 2: Illustration of three different potential dependent processes that can be effectively modeled by adiabatic DFT approaches: CO_2 adsorption, charge transfer reactions (e.g. $\text{H}^+ + \text{e}^- + * \rightarrow \text{H}^*$), and continuum charging/counter-charging.

The *local* potential drop at the interface, between the metal potential and the solution potential at the reaction plane, is the driving force for electrochemical reactions. This is the essential idea behind the Frumkin diffuse layer correction to reaction kinetics.^{81,82} As we

show below, this local potential drop is better approximated by the total effective surface charge than the overall work function. This concept is illustrated in Figure 3, where the potential drop across the electrochemical interface is illustrated. Here the work function is given by the potential difference between the metal surface and the vacuum level, $\Phi_M - \Phi_{\text{vac}}$. However, the driving force for charge transfer is instead described by $\Phi_M - \Phi_{\text{RP}}$, since the transition state lies in this region.

Figure 3: Illustration of the potential drop across the electrochemical interface. Here the surface (drawn as the left side of the plot), is covered by charge neutral solvent molecules (solid white circles) and anions (dark gray circles). Solvated cations form a Helmholtz like layer demarcating the outer Helmholtz plane, followed by the diffuse layer. The linear potential drop between the surface and the reaction plane gives the driving force for electron transfer ($\Phi_M - \Phi_{\text{RP}}$), while the work function is given by potential drop between the surface and the vacuum potential ($\Phi_M - \Phi_{\text{vac}}$).

In what follows, we derive a generic multi-capacitor model of the electrochemical interface,^{17,45,46,95–98} starting with the simple case of an interface with one charging component. We use this model to develop expressions relating electrochemical reaction energetics to both excess surface charge density, and the work function. We then show the “effective” surface

charge density to be the appropriate descriptor of the driving force, since it reflects the local potential drop. We demonstrate that, using the work function (a measure of the applied potential) as the descriptor, the reaction energetics are not uniquely defined. We then develop a framework to calculate electrochemical reaction energetics in general.

General Multi-Capacitor Model of the Electrochemical Interface

Energy of the Charged Interface

We first review the energy of the charged interface undergoing only one charging process. We can expand the energy as a Taylor expansion about a hypothetical zero interfacial charge $q = 0$, corresponding to a work function Φ_0 , as has been done in previous works.^{17,95–98}

$$E = E^0 + \left. \frac{\partial E}{\partial q} \right|_{q=0} q + \frac{1}{2} \left. \frac{\partial^2 E}{\partial q^2} \right|_{q=0} q^2 + \mathcal{O}(q^3) \quad . \quad (1)$$

Here $E^0 = E|_{q=0}$ is the energy of all *non-electrostatic* (i.e. chemical) components of the system at the hypothetical $q = 0$ case, which corresponds to the case of zero partial charges in Figure 2. This case is exemplified by, for instance, a hypothetical neutral H_3O molecule solvated above a metal slab (as opposed to a positively charged H_3O molecule solvated above a negatively charged metal slab), or a hypothetical adsorbed CO_2 molecule with no dipole moment.

By definition,

$$\left. \frac{\partial E}{\partial q} \right|_{q=0} = \Phi_0 \quad (2)$$

where Φ_0 is the work function at zero charge, referenced to the bulk electrolyte potential. We further assume here that we have a constant capacitance C , which we find to be valid in small potential ranges, as discussed later in this work:

$$\frac{\partial}{\partial q} \left(\frac{\partial E}{\partial q} \right) = \frac{\partial \Phi}{\partial q} = \frac{1}{C} \quad , \quad (3)$$

such that (1) becomes.

$$E = E^0 + q\Phi_0 + \frac{q^2}{2C} \quad . \quad (4)$$

We now use the capacitor equation $q = C(\Phi - \Phi_0)$ to write (1) in terms of Φ

$$E = E^0 + C(\Phi - \Phi_0)\Phi_0 + \frac{C(\Phi - \Phi_0)^2}{2} \quad . \quad (5)$$

Or without reference to the capacitance,

$$E = E^0 + q\Phi_0 + \frac{q(\Phi - \Phi_0)}{2} \quad . \quad (6)$$

As an example, we show the energetics of Pt (111) as a function of both excess surface charge q as well as the work function Φ in Figure 4. Here the surface was charged using the linearized-Poisson Boltzmann equation to place countercharge. The slight deviations from the model in panel (b) results from the capacitance being non-linear far from the potential of zero charge. From a linear fit of the surface charge as a function of potential, we calculate a surface capacitance C of $25 \mu\text{F cm}^{-2}$, and a potential of zero charge Φ_0 of 5.4 eV.

Figure 4: Energetics of Pt(111) as a function (a) excess implicit surface charge q , where dashed lines correspond to Eq. (4), and (b) work function Φ , where dashed lines correspond to Eq. (6). Panel (b) shows slight deviations far from the potential of zero charge (≈ 5.4 eV in this picture) due to the nonlinear capacitance behavior far from the PZC.

Reaction Energetics: Only One Charging Component

We now consider the energetics of an interfacial charge-transfer reaction, i.e. charging process of any of the envisioned capacitors in Figure 2. Considering an infinitely extended system, the charging and discharging of a single capacitor does not change the work function of the metal electrode. In a typically used finite unit cell setup, however, the charge-transfer reaction critically changes the electrode work function. As before, the hypothetical $q = 0$ state is one such that there is no charge separation; for example, a hypothetical neutral hydronium molecule solvated above an uncharged metal slab, or a hypothetical CO_2 molecule adsorbed with no dipole moment. We can therefore assume that Φ_0 does not change between the states considered. We find that in practice, the capacitance varies by only a very small amount for a large change in surface coverage, changing from $12.6 \mu\text{F cm}^{-2}$ for a clean Pt (111) surface to $10.1 \mu\text{F cm}^{-2}$ with CO_2 adsorbed in a 2×2 supercell, the smallest cell size considered here (and hence the highest coverage). This capacitance drop reduces to just $0.1 \mu\text{F cm}^{-2}$ in a 4×4 supercell, as we reported in a recent work.⁹⁰ We therefore assume that the capacitance between states does not vary.

Under these assumptions, from Eq. (4), we have the change in energy from state 1 to state 2 (denoted as subscript 1 and 2, respectively) as

$$\Delta E = \Delta E_0 + (q_2 - q_1)\Phi_0 + \frac{q_2^2 - q_1^2}{2C} \quad (7)$$

$$= \Delta E_0 + (q_2 - q_1) \left(\frac{\bar{q}}{A\tilde{C}} + \Phi_0 \right) \quad , \quad (8)$$

where we have defined the average charge $\bar{q} = \frac{1}{2}(q_1 + q_2)$ and introduced the surface area normalized capacitance, $\tilde{C} = C/A$. Eq. (8) can also be written as a function of work function via $q = C(\Phi - \Phi_0)$,

$$\Delta E = \Delta E_0 + (q_2 - q_1)\bar{\Phi} \quad , \quad (9)$$

where we have similarly defined $\bar{\Phi} = \frac{1}{2}(\Phi_1 + \Phi_2)$. In the example of CO_2 adsorption, $q_2 - q_1$

yields the effective surface charge associated with the a polarized CO₂ molecule. For the Volmer reaction, $q_2 - q_1$ yields the effective surface charge transferred. Naturally, $q_2 - q_1$ could also represent the charge difference via continuum charging of any surface composition.

In the limit of an infinitely sized simulation cell, the corresponding effect of the dipole shift on the potential and surface charge density is infinitesimal, i.e. $\Phi_1 \rightarrow \Phi_2$ and $q_1/A \rightarrow q_2/A$, but $q_1 \nrightarrow q_2$. In the infinite cell size limit, we have

$$\Delta E = \Delta E_0 + (q_2 - q_1) \left(\frac{q}{AC} + \Phi_0 \right) \quad (10)$$

$$= \Delta E_0 + (q_2 - q_1) \Phi \quad . \quad (11)$$

The effective charge $q_2 - q_1$ can be determined by evaluating the reaction energetics at multiple finite cell sizes and then fitting either Eq. 8 or Eq. 9, i.e.

$$q_2 - q_1 = \frac{\partial \Delta E}{\partial \Phi} = \frac{\partial \Delta E}{\partial \left(\frac{q}{AC} + \Phi_0 \right)} \quad . \quad (12)$$

This approach is equivalent to the cell extrapolation approach for constant potential reaction energetics, detailed in Ref. 44. Further details regarding this, and the choice of average work function as the descriptor can be found in the supporting information (SI) Note 1. There we explain that the change in energy as a function of average work function is equivalent to the cell-extrapolated energetics, where the work function does not change between the initial and final state. In the case of a simple proton-electron transfer, it has been shown in previous work that $q_2 - q_1$ can be usually be determined through the Bader^{78–80} charge of the slab and adsorbates (i.e. the charge extrapolation model).^{45,46}

The corresponding capacitance can be determined by fitting ΔE vs $\Phi_2^2 - \Phi_1^2$, since Eq. (9) can be written

$$\Delta E = \Delta E_0 + \frac{C}{2}(\Phi_2^2 - \Phi_1^2) \quad . \quad (13)$$

We note here that in the case of an adsorption reaction event, the calculated effective trans-

ferred charge $q_2 - q_1$ is not the charge *transferred* upon adsorption (i.e. the electrosorption valency^{92–94}), as seen in adsorption pseudocapacitances or in cyclic voltammetry. Rather, it is the physical charge separation at the interface that contributes to the corresponding capacitance of the given process.

To illustrate these charging behaviors, we have plotted the energetics of a simple proton-electron transfer process (Volmer, i.e. $(\text{H}^+ + \text{e}^-) + * \rightarrow \text{H}^*$) and CO_2 adsorption on Pt (111) as a function of the work function Φ in Figure 5. In this picture, no continuum solvation or charging is used; the different scatter points are achieved by changing the coverage of protons and CO_2 , respectively by changing the unit cell size.

Figure 5: Energy as a function of average work function, $\bar{\Phi} = \frac{1}{2}(\Phi_{\text{IS}} + \Phi_{\text{FS}})$ for CO_2 adsorption on Pt (111) and the Volmer reaction (i.e. $(\text{H}^+ + \text{e}^-) + * \rightarrow \text{H}^*$) on Pt (111), with no continuum solvation. The different scatter points are calculated by changing the coverage of CO_2 and protons by, for instance, changing the cell size. Here the x-axis is the average work function between the initial and final state, and so the slopes in this plot correspond to a fit of q_{eff} as given in Eq. (12).

Reaction Energetics: Two Charging Components

We now consider the case of a reaction energy evaluated where a second charging component is present and constant throughout the reaction pathway. For example, a Volmer reaction event where a constant continuum charge q_{imp} or an additional co-adsorbate with effective charge q_{ad} is added to the two states considered. As we illustrated in a previous work,⁹⁰ the energetics obtained with a constant charge vs $\bar{\Phi}$ between the states considered are equivalent to the grand canonical energy difference at constant potential. The latter method of charging the interface to achieve constant potential has been applied to a wide variety of surface electrochemical reactions,^{75,99–101} since it allows a simple way to probe energetics across a large range of work functions.

For a general system with both implicit and explicit charging, by applying Eq. (7), we can expand the energy about $q_{\text{imp}} = 0$, giving a total reaction energy as the sum of contributions from both explicit and implicit charging,

$$\Delta E = \Delta E_{\text{exp}} + \Delta E_{\text{imp}} \quad (14)$$

$$= \Delta E_{\text{exp}} + q_{\text{imp},2}\Phi_2 - q_{\text{imp},1}\Phi_1 + \frac{q_{\text{imp},2}^2 - q_{\text{imp},1}^2}{2C_{\text{imp}}} \quad (15)$$

where ΔE_{exp} , the component arising from explicit charging, is given by Eq. (8). We introduced the capacitance associated with charging the interface with a continuum charge, C_{imp} and note that it need not equal the capacitance associated with charging the interface via other methods. We assume that the continuum charge q_{imp} is constant between initial and final state in accordance with constant charge calculations, i.e. $q_{\text{imp},1} = q_{\text{imp},2} = q_{\text{imp}}$. The

reaction energy then reduces to

$$\Delta E = \Delta E_{\text{exp}} + q_{\text{imp}} (\Phi_2 - \Phi_1) \quad (16)$$

$$= \Delta E_0 + (q_2 - q_1) \left(\frac{\bar{q}_{\text{exp}}}{C_{\text{exp}}} + \Phi_0 \right) + q_{\text{imp}} \left(\frac{q_2 - q_1}{C_{\text{exp}}} \right) \quad (17)$$

$$= \Delta E_0 + \frac{q_2 - q_1}{\tilde{C}_{\text{exp}}} \left(\frac{\bar{q}_{\text{exp}} + q_{\text{imp}}}{A} + \tilde{C}_{\text{exp}} \Phi_0 \right) \quad (18)$$

Effective Surface Charge Density as the Appropriate Descriptor of Driving Force

As we noted previously, two independent charging components need not have identical associated capacitances. Here, we demonstrate that unequal capacitances lead to the average work function not uniquely defining the energetics, and that the surface charge density is a better descriptor of the local driving force.

To write Eq. (18) in terms of potential, we first write

$$\frac{\bar{q}_{\text{exp}}}{C_{\text{exp}}} + \Phi_0 = \frac{\Phi_2 - \Phi_0 + \Phi_1 - \Phi_0}{2} + \Phi_0 = \bar{\Phi}_{\text{exp}} \quad , \quad (19)$$

and note that

$$q_{\text{imp}} = C_{\text{imp}}(\Phi_{\text{imp},2} - \Phi_2) = C_{\text{imp}}(\Phi_{\text{imp},1} - \Phi_1) \quad (20)$$

$$= C_{\text{imp}} \left(\frac{\Phi_{\text{imp},2} + \Phi_{\text{imp},1}}{2} - \frac{\Phi_2 + \Phi_1}{2} \right) \quad (21)$$

$$= C_{\text{imp}}(\bar{\Phi}_{\text{imp}} - \bar{\Phi}_{\text{exp}}) \quad . \quad (22)$$

Inserting this expression into Eq. (18), we arrive at the reaction energy as a function of potential,

$$\Delta E = \Delta E_0 + (q_2 - q_1) \left[\bar{\Phi}_{\text{exp}} + \frac{C_{\text{imp}}}{C_{\text{exp}}} (\bar{\Phi}_{\text{imp}} - \bar{\Phi}_{\text{exp}}) \right] \quad (23)$$

Equation (23) demonstrates that, if the ratio C_{imp}/C is non-unity, the average potential

does not uniquely describe the reaction energy. In other words, for a given potential, the reaction energy can take on multiple values depending on the charging method used to achieve that potential.

We demonstrate this finding with two examples: the Volmer reaction, and CO_2 adsorption shown in Figure 6. We systematically modify the potential by varying both the explicit charge (i.e. changing the cell size and proton/ CO_2 coverage) as well as with continuum charge. A third example, CO_2 adsorption with varying co-adsorbates, can be found in SI Note 2. Figure 6 (a) shows that the reaction energy for Volmer is not uniquely determined by the potential, because the capacitance associated with explicit charging ($C_{\text{exp}} \approx 20 \mu\text{F cm}^{-2}$) and continuum charging ($C_{\text{imp}} \approx 9 \mu\text{F cm}^{-2}$) are significantly different. We note that these capacitances are fit via $q = C(\Phi - \Phi_0)$, as described in the first section. In contrast, Figure 6 (b) shows the reaction energy associated with CO_2 adsorption as a function of potential, similarly modifying the potential both with explicit (i.e. CO_2 coverage) and continuum charging. The agreement between continuum and explicit charging in this picture is much better, since the capacitance for each associated process is approximately identical ($C_{\text{exp}} \approx 12 \mu\text{F cm}^{-2}$, $C_{\text{imp}} \approx 14 \mu\text{F cm}^{-2}$).

Figure 6: Reaction energetics of CO_2 adsorption and the Volmer reaction as a function of (a) the average work function, corresponding to the potential as the descriptor for the driving force, as in Eq. (9). Panel (b) shows the same data set with the driving force given instead by the effective surface charge, $\frac{1}{A}(\bar{q} + q_{\text{imp}})$, as expressed in Eq. (18).

Figure 6 (b) then shows the energetics as a function of the effective surface charge density, corresponding to Eq. (18). Here it can be seen that regardless of the variation in capacitance, the energetics are uniquely defined. Since the capacitance for the two processes in the case of CO₂ adsorption are similar, the level of noise reduction is minimal. However, for the case of the Volmer reaction, the clearly non-collinear lines collapse onto a single line. This result is because the capacitance associated with the two charging processes, i.e. explicit proton coverage and continuum countercharge concentration, are quite different ($C_{\text{exp}} \approx 20\mu\text{F cm}^{-2}$, $C_{\text{imp}} \approx 9\mu\text{F cm}^{-2}$). As expressed in Eq. (23), this causes the energetics to not be uniquely described by the average work function. However, this challenge is mitigated when the same data set is instead plotted as a function of the effective surface charge. In contrast, because the capacitances associated with CO₂ adsorption and the placement of continuum countercharge are quite similar, this behavior is not as clearly seen.

In principle, in the special case where the capacitance of all components are equal, then the work function again would provide single-valued functions of energy (see SI Note 3). However, tuning the parameters in the models to do so would also affect the non-electrostatic terms in the energy, such as the solvation energy. Therefore, the reparametrization of every new electrochemical process to be modeled to retain a constant capacitance would both be cumbersome and lead to inconsistent solvation parameters.

We note that although we chose subscripts *exp* and *imp* in our derivation of the model for energetics with two charging components, the model is not specific to explicit and implicit charging. An example of this model working for a case with no implicit charging is illustrated in SI Note 2, where we show the binding energy of CO₂ (charging component 1) with various co-adsorbed ions (charging component 2). In this case, there is a charge associated with CO₂ denoted q_{CO_2} and a charge associated with the co-adsorbate denoted q_{ion} , which replaces subscripts *exp* and *imp* in our derivation.

Insensitivity of the Driving Force to Water Structure

An additional challenge associated with describing the reaction energetics as a function of work function arises for the case of explicit solvation. For a given charge state, the work function of a surface can vary dramatically simply due to the varying sum of water dipoles being exerted on the surface. However, the dipole associated with a given water structure does not affect the reaction energetics. We demonstrate this in Figure 7, which shows the electric field between the surface and the first water layer for two different water structures. We calculate the field as^{40,70}

$$E_{\text{field}} = -\frac{dV_{\text{diff}}}{dz} \quad , \quad (24)$$

where the potential difference V_{diff} is defined as

$$V_{\text{diff}} = V_{\text{total}} - V_{\text{electrolyte}} - V_{\text{slab}} \quad . \quad (25)$$

Here V refers to the local electrostatic (ionic and Hartree) potential output by DFT. The subscript *total* refers to the local potential of the entire system, *electrolyte* refers to the local potential of just the electrolyte, and *slab* refers to the local potential of just the slab. This field reflects the local potential drop that would drive an electrochemical reaction or a chemical reaction involving polar adsorbates. In this picture, the first water layer is fixed while three water layers above have adopted different configurations that result in a nearly 4 eV shift in the work function. Further details regarding the generation of these data can be found in Note 4 in the SI. Specifically, we demonstrate that the reaction energetics are insensitive to the change in work function associated with the changing water dipoles.

Figure 7: Electric field taken in a slice between the surface and the first water layer. Despite a nearly 4 eV difference in the work function between the left and right panels, the electric field at the interface is virtually identical, since the surface charge is roughly the same.

Insensitivity of the Driving Force to Continuum Charge Distribution

Another consequence of the effective surface charge density being the descriptor of driving force is the insensitivity of reaction energetics to the countercharge placement. In recent years, many different models of the electrolyte distribution have emerged, which have been shown to reproduce experimental capacitance curves at varying degrees of accuracy.^{17,50–55,57–63,102} These charge placement models can have a significant effect on the measured capacitance ranging from 13 to 18 $\mu\text{F cm}^{-2}$ (see SI Note 5) and potential of zero charge, and hence the predicted reaction energetics as a function of work function. However, as a function of surface charge, the energetics are largely insensitive. To demonstrate this, we have calculated the binding energy of two CO molecules on Cu (100) and Cu (211) using three countercharge placement models: planar countercharge, linear modified Poisson-Boltzmann, and modified Poisson-Boltzmann, as implemented in Environ.^{47,103,103} Figure 8 illustrates that there is less than 10 meV variation in the reaction energetics as a function of surface charge for the two facets. Note that the abscissa in 8(a) is not the effective surface charge, but just the surface charge due to continuum charging. However, because the charge due to CO is quite small, the effective surface charge is dominated by the continuum charging, and so we neglect to include the contribution of CO binding to the surface charge.

Figure 8: Illustration of the insensitivity of reaction energetics to the countercharge placement model. (a) Binding energy of two CO molecules on Cu (100) and Cu (211) as a function of surface charge for the three charge placement models. (b) Binding energy of two CO molecules on Cu (100) and Cu (211) as a function of work function. The nonlinear behavior observed for Cu (211) is due to a change in binding configuration as the surface charge is made more negative.

General Framework for Calculation of Electrochemical Reaction Energetics

The models developed in this work can be applied to a general surface electrochemical reaction using a simple framework, illustrated in Figure 9.

Figure 9: Flowchart illustrating the general framework for calculating electrochemical reaction energetics with the models presented in this work.

The first step, determining the effective charge q_{eff} , is equivalent to calculating the slope of the lines shown in Figure 5. Then, determining the energetics as a function of the effective surface charge is equivalent to Figure 6 (b), where we show the Volmer reaction and CO_2 adsorption as a function of the total effective surface charge. The capacitance for each charging process (in the case of Figure 6 (b), explicit and implicit charging) can be calculated by, for instant, fitting $q = C(\Phi - \Phi_0)$, or equivalently, fitting Eq. 13. Among the two model reactions shown, only CO_2 adsorption satisfies the criteria that each capacitance is equivalent to the overall capacitance, and so the energetics as a function of charge can be directly converted to the energetics shown in Figure 6 (a). Here, the energetics are uniquely determined by the potential. However, for the second case, the Volmer reaction

(i.e. $(\text{H}^+ + \text{e}^-) + * \rightarrow \text{H}^*$), it cannot be assumed that the two capacitances are equivalent to the overall capacitance, since they are quite different ($C_{\text{exp}} \approx 20 \mu\text{F cm}^{-2}$, $C_{\text{imp}} \approx 9 \mu\text{F cm}^{-2}$). Here, assuming an equivalent capacitance yields the energetics shown in Figure 6 (a), where it is clear that the energetics are not uniquely determined by the work function. Instead, the capacitance can be taken from an experimental charging curve for Pt (111), where it is found to have a capacitance of roughly $C \approx 20 \mu\text{F cm}^{-2}$.¹⁰⁴ For potentials far from the potential of zero charge, a more detailed charging function ($\Phi = f(q)$ for some f) could easily be substituted in lieu of the constant capacitance frequently reported in the literature (i.e. $\Phi = \frac{1}{C}q + \Phi_0$). With the energetics as a function of potential determined, they can then be input into a micro-kinetic model to determine, for instance, rates of electrochemical processes as a function of potential.

Conclusions

In this work, we have developed a general framework for the calculation of electrochemical reaction energetics from simulations of both explicit and implicit electrolyte. We demonstrate that the electrochemical interface can be effectively modeled as multiple capacitors, each corresponding to the separate charging components (i.e. separate dipole-field interactions). We show that an effective surface charge density, rather than the traditionally considered work function, is the appropriate descriptor for the driving force of electrochemical reactions. We illustrate this finding with examples of models of the Volmer reaction and CO_2 adsorption. This framework allows us to, for the first time, effectively model the electrochemical interface using a hybrid explicit/continuum model in a way that is not dependent on cell size. These hybrid models are becoming increasingly popular as a way to treat the electrolyte in surface electrochemistry, since they allow for explicit treatment of charge in charge transfer reactions, without the need for sampling of solvent states. They furthermore provide a simple way to probe large ranges of potential, without the need for

costly extrapolation techniques. Future work will apply this method to reactions occurring in basic conditions, which previously was complicated by the aforementioned band misalignment challenges⁶⁸ with charged species at the interface, in addition to the usual challenges of sampling that occur with a purely explicit treatment of the electrolyte. Taken together, this work represents a significant advancement in the ability of modern computational tools to investigate surface electrochemical phenomena through the use of hybrid explicit/continuum solvation models coupled with DFT.

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Graphical TOC Entry

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Supporting Information: Unified approach to implicit and explicit solvent simulations of electrochemical reaction energetics

Joseph A. Gauthier,^{†,‡} Colin F. Dickens,^{†,‡} Hendrik H. Heenen,[¶] Stefan Ringe,^{‡,†}
and Karen Chan*,[¶]

[†]*SUNCAT Center for Interface Science and Catalysis, Department of Chemical
Engineering, Stanford University, Stanford, California 94305, United States*

[‡]*SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator
Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, United States*

[¶]*Department of Physics, Technical University of Denmark, DK-2800, Kgs. Lyngby,
Denmark*

E-mail: kchan@fysik.dtu.dk

Note 1

In this note, we further explain the use of the average work function, $\overline{\Phi}$, as the descriptor for electrochemical reactions used in the main text.

In the main text, we establish that the energy depends quadratically on the surface charge density q and the potential Φ . That is, we assume that the capacitance is a constant function of potential and therefore the cubic term in the Taylor expansion is negligible (this is shown to be a good assumption in Figure 4). Expanding the energy as a function of q , we have

$$E(q) = E(q = 0) + q\Phi_0 + \frac{q^2}{2C} \quad . \quad (\text{S1})$$

We can write this instead as a function of potential by using the usual capacitance relation $q = C(\Phi - \Phi_0)$,

$$E(\Phi) = E(\Phi = \Phi_0) + C\Phi_0(\Phi - \Phi_0) + \frac{C}{2}(\Phi - \Phi_0)^2 \quad . \quad (\text{S2})$$

Seen in Figure S1 is a plot of the energy E as a function of the coverage θ of (in this case) protons. In general, the energy depends quadratically on both θ and work function Φ .¹ In practical density functional theory (DFT) calculations of relative energies between two different states of θ or Φ , the change in energy calculated is not equal to $dE/d\theta$. Instead it is equal to $\Delta E/\Delta\theta$, since the coverage changes substantially between the initial and final state. This is illustrated in Figure S1, where the blue dashed line indicates the energy change between two DFT calculations with different coverages ($\theta=0$ and 0.5). What one would like to calculate though is instead the instantaneous derivative, in order to relate energy differences to a coverage or work function. Toward this end, we take advantage of a property of parabolas, for which the slope of a secant line is equivalent to the slope of the tangent at the average value of the independent variable. For a general parabola $f(x) = c_1x^2 + c_2x + c_3$,

the slope of a secant line from point a to b is given by

$$\begin{aligned}\frac{\Delta f(x)}{\Delta x} &= \frac{f(b) - f(a)}{b - a} \\ &= \frac{c_1(b^2 - a^2) + c_2(b - a)}{b - a} \\ &= c_1(b + a) + c_2 \quad .\end{aligned}\tag{S3}$$

The slope of the tangent line at a given point x is then given by

$$\frac{df}{dx} = 2c_1x + c_2 \quad .\tag{S4}$$

Equating (S3) and (S4), we see that the slope of the tangent line and secant line are equivalent for the tangent to the average of a and b , i.e.

$$\frac{df}{dx}\left(x = \frac{a + b}{2}\right) = \frac{f(b) - f(a)}{b - a} \quad .\tag{S5}$$

Figure S1: Graphic explanation of the average work function being used to describe reaction energetics. In this graphic, the coverage of protons θ is used to illustrate the concept. Since the energy E depends quadratically on θ , the slope of the secant line between two points θ_1 and θ_2 is exactly equal to the slope of the tangent line at $\theta = \bar{\theta}$.

In the context of Figure S1, this means that the change in energy calculated between two states in a standard DFT calculation (in the Figure, going from $\theta = 0$ to $\theta = 0.5$) is equivalent to the DFT calculation with no change in coverage between initial and final states (i.e. cell-extrapolated), at a coverage of $\theta = \bar{\theta} = 0.25$.

Because the energy also depends quadratically on the work function Φ , the same argument is made. The change in energy as calculated by DFT in a finite cell, which results in a change in work function $\Phi_1 \rightarrow \Phi_2$, is exactly equivalent to the calculation with no change in work function, at the average work function. By analogy to Eq. (S5),

$$\frac{dE}{d\theta}(\theta = \bar{\theta}) = \frac{E(\theta_2) - E(\theta_1)}{\theta_2 - \theta_1} \quad (\text{S6})$$

$$\frac{dE}{d\Phi}(\Phi = \bar{\Phi}) = \frac{E(\Phi_2) - E(\Phi_1)}{\Phi_2 - \Phi_1} \quad (\text{S7})$$

Note 2

Here we illustrate a third example of surface charge as the descriptor for the driving force of charge transfer processes. Shown in Figure S2 is the binding energy of two CO₂ molecules as both a function of the average work function, and as a function of the average effective charge. Note that the binding energy for two CO₂ molecules is shown because a cell symmetric in the z -coordinate was used.

Figure S2: Binding energy of CO₂ on Pt (111) with various coadsorbates to modify the work function. (a) ΔE_{CO_2} as a function of the average work function. (b) ΔE_{CO_2} as a function of the effective surface charge. The solid black line represents a best fit to all data points.

As can be seen in Figure S2(a), the data shows a significant amount of noise. This is due largely to the chemical interaction between the coadsorbate and CO₂ on the surface. We note that the scale on the y-axis is rather small, and so the average deviation remains quite small overall. Figure S2(b) shows some reduced noise, with all slopes having the same sign. As outlined in the main text, the effective charge q_{eff} , due to the ion (and CO₂) is determined via

$$q_{\text{eff}} = \frac{\partial \Delta E_{\text{ion}}}{\partial \bar{\Phi}} \quad . \quad (\text{S8})$$

Note 3

In this note, we discuss tuning the capacitance of the implicit model, such that it matches that of the overall process. In principle this would mitigate the issues presented in the main text, where the work function acts as a poor descriptor for the driving force. If the capacitance for every charging process in the system is the same, then the work function can act as a descriptor. We found that using a partial bilayer of explicit solvent (rather than a full bilayer), equivalent to only one water molecule to stabilize each hydronium ion, lowered the capacitance due to explicit protons.

Figure S3: Illustration of capacitance tuning for (a) proton creation and (b) the Volmer reaction. Here the dashed colored lines correspond to different fixed proton concentrations, with the work function being modified by changing the continuum countercharge. The dashed line corresponds to the case of zero continuum countercharge, with the work function being modified by changing the explicit proton coverage (i.e. cell extrapolation).

As can be seen in Figure S3, using a very sparse bilayer sufficiently lowers the capacitance of explicit charging, to the point that it roughly matches that of implicit charging. This results in the work function acting as a better descriptor for the driving force, as evidenced by the lines for implicit and explicit charging being approximately parallel and having similar

intercepts. Figure S4 illustrates the problem with this approach of tuning the capacitance. Here we plot the Volmer reaction energy as a function of (a) the proton coverage θ and (b) work function Φ .

Figure S4: Illustration of the problem using an incomplete bilayer to tune the capacitance. (a) Change in Volmer reaction energy as a function of the coverage of protons. (b) Change in Volmer reaction energy as a function of the work function. With an incomplete bilayer, $\partial \Delta^2 E_{\text{Volmer}} / \partial \bar{\Phi}^2$ is equivalent to the case with no implicit solvent, indicating equivalent capacitance. However, $\partial^2 \Delta E_{\text{Volmer}} / \partial \bar{\theta}^2$ is significantly reduced with the incomplete bilayer, indicating a reduced proton-proton interaction.

As we showed earlier in Note 1, the points in the above plots are exactly equivalent to the instantaneous derivatives. That is, the points in Figure S4(a) correspond to $\partial E / \partial \theta$, while the points in Figure S4(b) correspond to $\partial E / \partial \Phi$, and therefore the slope of the lines correspond to $\partial^2 E / \partial \theta^2$ and $\partial^2 E / \partial \Phi^2$ respectively. Using the chain rule, we can write

$$\frac{\partial^2 E}{\partial \Phi^2} = \frac{\partial^2 E}{\partial \theta^2} \left(\frac{\partial \theta}{\partial \Phi} \right)^2 \quad (\text{S9})$$

In a 6x3 supercell of Pt (111), we calculated from DFT the change in work function upon the removal of a proton from the water bilayer (i.e. via the Volmer reaction), tabulated in

Table S1.

Table S1: Calculated changes in work function across Volmer reaction coordinate in a 6x3 supercell of Pt (111)

Case	$\Delta\Phi$ / eV
Implicit, full bilayer	0.26
Implicit, incomplete bilayer	0.32
No implicit, full bilayer	0.79
No implicit, incomplete bilayer	0.84

Because the cell size is the same for each of these cases, these numbers can be used as approximations to a number proportional to the inverse of the instantaneous proton dipole moment, $\partial\theta/\partial\Phi$,

$$\frac{\partial\Phi}{\partial\theta} \propto \Delta\Phi \quad (\text{S10})$$

Returning to Figure S4(b), we can see that the slope of the line corresponding to an incomplete bilayer is the same as that of the case with no continuum solvation, which explains the reasonable agreement in Figure S3. However, as seen in Figure S4(a) since the slope of the line corresponding to an incomplete bilayer is different than the other cases, this means that using an incomplete bilayer changes $\partial^2 E/\partial\theta^2$, which represents the proton-proton interaction. In other words, while the use of an incomplete bilayer does in fact change the capacitance in a way that allows the work function to be used as the descriptor, it does so by decreasing the interaction between protons, i.e. the explicit capacitance.

Ideally, the capacitance would instead be tuned the other way, without affecting the proton-proton interaction and instead increasing the capacitance associated with continuum charging. This in principle could be done by for example changing the parameters built into the continuum model. However this would necessarily affect other factors in the system, such as the solvation energy. It would also not be easily generalizable to new systems, and would have to be fit for each case, limiting its use in practice.

Note 4

Here we expand upon the methods used to generate the data found in Figure 7 in the main text.

In Figure S5, we show the Volmer reaction energy, with no continuum solvation, for varying water structures at each point.

Figure S5: Volmer reaction energy as a function of work function for approximately 100 different water structures. The first water bilayer is identical for each point, while the three layers above change for each point. Despite a more than 3 eV change in the work function, the range of Volmer reaction energies varies by less than 0.3 eV.

As can be seen in Figure S5, there is a wide range of work function and yet only a small range of energies. The small amount of scatter is likely due to very slightly different water structures between initial and final state. The picture in this system is directly analogous to the Frumkin correction, where only the potential drop between the electrode and the inner Helmholtz plane (IHP) contributes to the electron transfer driving force. Here, only the potential drop between the electrode and the first solvent bilayer contributes to the reaction driving force; the changes in measured work function convolute this potential drop and the

potential drop due to water dipoles. This results in a huge variation of work function, but with very little change in driving force.

To generate the different water structures, the first water bilayer and the entire Pt (111) slab were fixed, and the top three water bilayers then underwent 5 picoseconds of ab-initio molecular dynamics (AIMD). A Nosé thermostat (IBRION = 0, SMASS = 3) was used to control the temperature, with a set point of 300 K, and a time-step of 1 picosecond (POTIM = 1.). Van der Waals interactions were accounted for using the damped DFT-D3 correction of Grimme^{2,3} (IVDW = 11). From the MD trajectory, snapshots were taken every 20 femtoseconds. The water structure in the top three layers was relaxed above the initial and final state of the Volmer reaction, where the first bilayer was fixed to avoid chemical effects convoluting the energetics. This then gives approximately 250 Volmer reaction energies, each with a different water structure. The mean square displacement between the initial and final state were calculated illustrated in Figure S6.

Figure S6: Histogram illustrating the mean square displacement between initial and final states for the 254 Volmer reaction energies calculated.

The purpose of this exercise is to illustrate that, when holding chemical effects (e.g.

hydrogen bonding, solvation) constant, the contribution of the changed water structure to the driving force of the reaction is negligible. To this end we did not include the energies associated with any water structure where the initial state and final state differed by a mean square displacement of greater than 0.5 Å. We note that including all trajectories does not significantly change the slope of the line shown in Figure 7 in the main text, going from 0.036 to 0.047 by including every water structure. However, the range of energies (that is, the highest ΔE_{Volmer} minus the lowest ΔE_{Volmer}) does change somewhat, illustrated in Figure S7. This can be explained by the change in water structure between initial and final state causing a change in the chemical effects we presume to be constant.

Figure S7: Range of energies (highest ΔE_{Volmer} minus lowest ΔE_{Volmer}) as a function of the cutoff mean square displacement.

Note 5

Here we show the capacitance curves associated with our illustration that the reaction energetics are insensitive to the countercharge placement model chosen. Figure S8 illustrates that the capacitance can change somewhat significantly, which corresponds to a significant

difference in energetics as a function of potential.

Figure S8: Capacitance curves for Cu (211) and Cu (100) with three charge placement models: the modified Poisson-Boltzmann (MPB) and its linearized version (LMPB) and a planar counter-charge (PCC).

References

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Tables and data corresponding to figures from the main text

Here we provide tables and input files necessary to reproduce all figures from the main text.

Figures 1-3

The data used in the plots of Figure 1 have deliberately arbitrary units and so no values are provided. Figures 2 and 3 are similarly explanatory schematics with no data to provide.

Figure 4

Data corresponding to Figure 4:

E / eV	$q / \mu\text{C cm}^{-2}$	Φ / eV
3.59217955516	-34.8284051634	6.54577080861
2.94602229419	-29.0236709695	6.37106408838
1.11745081766	-11.6094683878	5.79784938832
0.547778509728	-5.80473419391	5.58565829728
0.0	0.0	5.36309412301
-0.524280672303	5.80473419391	5.13279412303
-1.02469150461	11.6094683878	4.89749412305
-2.37164365156	29.0236709695	4.09759412312
-2.76694917388	34.8284051634	3.82759412314

Geometry input (POSCAR):

Pt

1.0000000000000000

5.6416157967247482 0.0000000000000000 0.0000000000000000

-2.8208078983623746 4.8857825983552177 0.0000000000000000

0.0000000000000000 0.0000000000000000 16.9312444075633444

Pt

16

Selective dynamics

Direct

0.0000000000000000	0.0000000000000000	0.2953120207612443	T	T	T
0.3333333333333357	0.1666666666666643	0.4319843258704026	F	F	F
0.1666666666666643	0.3333333333333357	0.5680156741295903	F	F	F
0.5000000000000000	0.0000000000000000	0.7046879792387557	T	T	T
0.0000000000000000	0.5000000000000000	0.2953120207612443	T	T	T
0.3333333333333357	0.6666666666666643	0.4319843258704026	F	F	F
0.1666666666666643	0.8333333333333357	0.5680156741295903	F	F	F
0.5000000000000000	0.5000000000000000	0.7046879792387557	T	T	T
0.5000000000000000	0.0000000000000000	0.2953120207612443	T	T	T
0.8333333333333357	0.1666666666666643	0.4319843258704026	F	F	F
0.6666666666666643	0.3333333333333357	0.5680156741295903	F	F	F
0.0000000000000000	0.0000000000000000	0.7046879792387557	T	T	T
0.5000000000000000	0.5000000000000000	0.2953120207612443	T	T	T
0.8333333333333357	0.6666666666666643	0.4319843258704026	F	F	F
0.6666666666666643	0.8333333333333357	0.5680156741295903	F	F	F
0.0000000000000000	0.5000000000000000	0.7046879792387557	T	T	T

VASP input file (INCAR):

INCAR created by Atomic Simulation Environment

ENCUT = 500.000000

SIGMA = 0.050000

EDIFF = 0.0001

EDIFFG = -0.03

PREC = Accurate

GGA = RP
ALGO = Normal
ISMear = 0
NELM = 250
NSW = 1000
IBRION = 2
NCORE = 16
KPAR = 7
LVHAR = .TRUE.
POTIM = 0.2
LSOL = .TRUE.
LAMBDA_D_K = 3.0
TAU = 0
NELECT = 160.0

Note that for different charges, the entry "NELECT" was varied to produce the different data points.

Figure 5

Data corresponding to Figure 5:

ΔE_{CO_2} / eV	$\bar{\Phi}$ / eV
0.792935455	6.28890967801
0.770970825	5.97826231432
0.738200705	5.88380788214
0.74461845	5.89182506158
0.738964705	5.83729891305
0.75026978	5.79672813601

0.726125725	5.7424552028
0.70478197	5.69967657212
0.72697721	5.69418021333

$\Delta E_{\text{Volmer}} / \text{eV}$	$\bar{\Phi} / \text{eV}$
0.007504865	4.89874704757
0.007504865	4.89874704757
0.41209548	5.40688860091
0.41209548	5.40688860091
-0.49698839	4.45877079266
0.61101113	5.71845917931
-0.569108955	4.25263910041
0.72221029	6.05602074766
-0.6297205	4.0919129468
0.865047195	6.2688255888

INCAR file used for all relaxations:

INCAR created by Atomic Simulation Environment

ENCUT = 500.000000

SIGMA = 0.050000

EDIFF = 1.00e-04

EDIFFG = -3.00e-02

PREC = Accurate

GGA = RP

ALGO = Normal

ISMEAR = 0

NELM = 250
 IBRION = 2
 NSW = 1000
 NCORE = 8
 LCHARG = .FALSE.
 LVHAR = .TRUE.
 POTIM = 0.2

Figure 6

Data corresponding to Figure 6:

$\Delta E_{\text{CO}_2} / \text{eV}$	$\bar{\Phi} / \text{eV}$	$\frac{\overline{q_{\text{exp}}} + \overline{q_{\text{imp}}}}{A} / \mu\text{C cm}^{-2}$
0.828276295904	6.49583282309	-18.98422594965748
0.759159431139	6.14206438771	-13.187515736021604
0.68698319	5.73174670785	-7.390805522385735
0.609809068873	5.28659732377	-1.5940953087498642
0.527712109267	4.80426334468	4.202614904886007
0.662830706404	5.63750003294	-4.218716877701725
0.64629998524	5.54816033602	-2.93055905244929
0.63054565	5.4486691568	-1.6424012271968547
0.613580105537	5.35092466013	-0.3542434019444195
0.596162021355	5.25031003708	0.9339144233080157
0.655021204929	5.66675165168	-4.752626121260275
0.637691037627	5.5608497206	-3.3014425727838552
0.61988995	5.45249300547	-1.850259024307435
0.601384484698	5.34162941458	-0.3990754758310153
0.5823098632	5.22829286981	1.0521080726454044
0.628624848854	5.56851868627	-3.164037658276294

0.616748694948	5.49756931374	-2.1979192893369675
0.604670905	5.42467993696	-1.2318009203976412
0.592208413022	5.35143035821	-0.2656825514583149
0.579540496008	5.2759801734	0.7004358174810115
0.622193209356	5.50065365697	-2.1093584388508626
0.610934092943	5.45866764064	-1.465279526224645
0.603850005	5.40769888684	-0.8212006135984273
0.595544993331	5.3583025981	-0.17712170097220975
0.587245114004	5.30774025542	0.46695721165400783
0.671657481053	5.75010709701	-6.328075316552487
0.646179401271	5.6041674754	-4.395838578673864
0.621835495	5.47060795729	-2.4636018407952425
0.591609087227	5.32983210385	-0.5313651029166206
0.56354714075	5.1830535637	1.4008716349620012
0.593897902674	5.6049490798	-3.996679147296306
0.57678212967	5.51764258813	-2.7763191023203344
0.56015639	5.43087294754	-1.5559590573443633
0.543429494099	5.34125882391	-0.33559901236839207
0.526641696634	5.25017264956	0.8847610326075792
0.605771838073	5.52015123547	-2.8124779184677715
0.592672531753	5.45641443438	-1.9537060349661615
0.58310706	5.39182693452	-1.094934151464552
0.566062275784	5.32740140522	-0.23616226796294246
0.55243641026	5.26183996155	0.6226096155386671
0.689813625067	6.01435067712	-10.848129114089977
0.646357171949	5.79531694574	-7.535723277726625
0.603153745	5.56737224341	-4.223317441363274

0.558102688292	5.34260847179	-0.9109116049999221
0.514959956987	5.07329868242	2.4014942313634298

$\Delta E_{\text{Volmer}} / \text{eV}$	$\bar{\Phi} / \text{eV}$	$\frac{\overline{q_{\text{exp}}} + \overline{q_{\text{imp}}}}{A} / \mu\text{C cm}^{-2}$
0.413841084168	5.45765	5.8266235333340495
0.232051412662	4.9584	7.3400322432909455
0.0432996742747	4.3851	8.853440953247842
-0.1410884464	3.7734	10.36684966320474
-0.31470211713	3.1619	11.880258373161636
0.906838522791	5.63425	2.9133117666670247
0.802680585854	5.34565	3.6700161216454728
0.691814566293	5.0264	4.426720476623921
0.577374433356	4.68915	5.18342483160237
0.461897614678	4.34555	5.940129186580818
1.10503628531	5.8505	1.4566558833335124
1.05101780837	5.70375	1.8350080608227364
0.995422465683	5.5461	2.2133602383119606
0.937583068087	5.3818	2.591712415801185
0.889163911859	5.2121	2.970064593290409
1.00885672648	5.7751	1.942207844444683
0.941590998984	5.5837	2.4466774144303156
0.870267713821	5.37485	2.9511469844159475
0.79601573533	5.1519	3.4556165544015793
0.719870898858	4.92015	3.960086124387212
0.413839689583	5.4577	5.8266235333340495
0.232049303777	4.95845	7.3400322432909455
0.0433002185036	4.3851	8.853440953247842

-0.14108569125	3.77335	10.36684966320474
-0.31470051846	3.16185	11.880258373161636
-0.310761602446	4.54255	11.766752719914868
-0.41748400834	4.2351	12.523457074893317
-0.519474082263	3.92145	13.280161429871765
-0.615820480911	3.6061	14.03686578485021
-0.706223504891	3.2947	14.793570139828661
-0.64176007385	3.91245	14.736817313205277
-0.683218761871	3.76175	15.115169490694502
-0.723228851806	3.61175	15.493521668183725
-0.761750274913	3.46165	15.871873845672948
-0.798805276449	3.3118	16.250226023162174
-0.514855119713	4.1214	13.746795782108473
-0.577191300734	3.91815	14.251265352094103
-0.63700702721	3.714	14.755734922079737
-0.69419852172	3.51005	15.26020449206537
-0.748686769221	3.3074	15.764674062051002

Figure 7

POSCAR file corresponding to high work function case:

Pt H O

1.0000000000000000

8.4638399999999994 0.0000000000000000 0.0000000000000000

0.0000000000000000 4.8865999999999996 0.0000000000000000

0.0000000000000000 0.0000000000000000 32.1040899999999993

Pt H O

18 33 16

Selective dynamics

Direct

0.0000000000000000 0.0833333300000021 0.2180407600000009 F F F
0.3333333300000021 0.0833333300000021 0.2180407600000009 F F F
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0.9985927700000019 0.4220822600000034 0.3635304200000036 F F F
0.3321781400000035 0.4215228600000032 0.3622850900000003 F F F
0.6658156000000020 0.4204424099999997 0.3622405099999995 F F F
0.1662878400000025 0.9220588900000024 0.3627106799999993 F F F
0.4995918899999978 0.9204650699999988 0.3628199999999993 F F F
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0.0294431399999979 0.2691702600000028 0.4674948400000005 F F F
0.9653096400000010 0.4541662000000031 0.4291165899999996 F F F
0.8369284199999996 0.4285194400000023 0.4730057299999970 F F F
0.4273882600000007 0.9438308000000006 0.4723800299999965 F F F
0.5432503899999972 0.9345016600000022 0.4348752300000029 F F F
0.1040323000000001 0.8282137500000033 0.4717710199999985 F F F

0.1736816100000027 0.9956579899999980 0.4352335800000020 F F F
 0.6313659599999966 0.2664434599999979 0.4787605400000032 F F F
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INCAR file corresponding to high work function case:

INCAR created by Atomic Simulation Environment

ENCUT = 500.000000

SIGMA = 0.050000

EDIFF = 1.00e-04

EDIFFG = -5.00e-02

PREC = Accurate

GGA = RP

ALGO = Normal

ISMEAR = 0

NELM = 250
 IBRION = 2
 NSW = 0
 NCORE = 16
 KPAR = 14
 LWAVE = .FALSE.
 LVHAR = .TRUE.
 LDIPOL = .TRUE.
 IDIPOL = 3
 DIPOL = 0.5 0.5 0.5

POSCAR file corresponding to low work function case:

Pt H O

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8.4638399999999994 0.0000000000000000 0.0000000000000000

0.0000000000000000 4.8865999999999996 0.0000000000000000

0.0000000000000000 0.0000000000000000 32.1040899999999993

Pt H O

18 33 16

Selective dynamics

Direct

0.0000000000000000 0.0833333300000021 0.21804076000000009 F F F

0.3333333300000021 0.0833333300000021 0.21804076000000009 F F F

0.6666666999999979 0.0833333300000021 0.21804076000000009 F F F

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0.5000000000000000 0.5833333300000021 0.21804076000000009 F F F

0.8333333300000021 0.5833333300000021 0.21804076000000009 F F F

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 0.4995918899999978 0.9204650699999988 0.3628199999999993 F F F
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 0.6313659599999966 0.2664434599999979 0.4787605400000032 F F F
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INCAR file corresponding to low work function case:

INCAR created by Atomic Simulation Environment

ENCUT = 500.000000

SIGMA = 0.050000

EDIFF = 1.00e-04

EDIFFG = -5.00e-02

PREC = Accurate

GGA = RP

ALGO = Normal

ISMEAR = 0

NELM = 250

IBRION = 2

NSW = 0

NCORE = 16

KPAR = 14

LWAVE = .FALSE.

LVHAR = .TRUE.

LDIPOL = .TRUE.

IDIPOL = 3

$$\text{DIPOL} = 0.5 \ 0.5 \ 0.5$$

Figure 8

Data corresponding to Figure 8:

$2\Delta E_{\text{CO}}$ (Lin. Mod. PB) / eV	Facet	q / $\mu\text{C cm}^{-2}$	$\overline{\Phi}$ / eV
-1.4563549651975336	211	-25.563257651181587	2.4116999999999997
-1.3756121224760136	211	-19.17244323838619	2.9161
-1.3285761570114119	211	-12.781628825590793	3.2227
-1.3215146668408124	211	-6.390814412795397	3.66655
-1.3133663539992995	211	0.0	4.07425
-1.1604698058217764	100	-15.654234352173216	2.99235
-1.119176802916627	100	-11.740675764129913	3.30785
-1.0760934950449155	100	-7.827117176086608	3.6059
-1.034064628292981	100	-3.913558588043304	3.88545
-0.9888406688842224	100	0.0	4.1495

$2\Delta E_{\text{CO}}$ (Planar CC) / eV	Facet	q / $\mu\text{C cm}^{-2}$	$\overline{\Phi}$ / eV
-1.4557301237909996	211	-25.563257651181587	2.5985500000000004
-1.3760662804706953	211	-19.17244323838619	3.04835
-1.3269396643881919	211	-12.781628825590793	3.3169
-1.3205175737093668	211	-6.390814412795397	3.7104
-1.313004374565935	211	0.0	4.0753
-1.1610345100634731	100	-15.654234352173216	3.1329000000000002
-1.122760542173637	100	-11.740675764129913	3.41075
-1.0815117577731144	100	-7.827117176086608	3.6702
-1.037887623642746	100	-3.913558588043304	3.91815
-0.9956928354804404	100	0.0	4.15185

$2\Delta E_{\text{CO}}$ (Mod. PB) / eV	Facet	q / $\mu\text{C cm}^{-2}$	$\bar{\Phi}$ / eV
-1.1557542090595234	100	-15.654234352173216	3.07875
-1.1162746408081148	100	-11.740675764129913	3.3621499999999997
-1.075886484439252	100	-7.827117176086608	3.63065
-1.03174220470828	100	-3.913558588043304	3.89095
-0.9893668690201594	100	0.0	4.15075
-1.4118651689204853	211	-22.367850444783887	2.8058
-1.3731766355922446	211	-19.17244323838619	3.02855
-1.3273621211192221	211	-12.781628825590793	3.28355
-1.3215508579851303	211	-6.390814412795397	3.68225
-1.3137836405694543	211	0.0	4.0732

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