Force-based method to determine the potential dependence in electrochemical barriers

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Abstract

Determining *ab-initio* potential dependent energetics are critical to investigating mechanisms for electrochemical reactions. While methodology for evaluating reaction thermodynamics is established, simulation techniques for the corresponding kinetics is still a major challenge owing to a lack of potential control, finite cell size effects or computational expense. In this work, we develop a model which allows for computing electrochemical activation energies from just a handful of Density Functional Theory (DFT) calculations. The sole input into the model are the atom centered forces obtained from DFT calculations performed on a homogeneous grid composed of varying field-strengths. We show that the activation energies as a function of the potential obtained from our model are consistent for different super-cell sizes and proton concentrations for a range of electrochemical reactions.

Introduction

Computational *ab-initio* investigations with Density Functional Theory (DFT) have provided the basis for the mechanistic understanding of several electrochemical reactions, such as the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER),¹⁻⁴ electrochemical CO₂ reduction (CO₂R),⁵⁻⁸ hydrogen evolution reaction (HER).⁹⁻¹² While reaction thermodynamics for reactions involving protonelectron transfers are readily captured by the computational hydrogen electrode,¹ accurately determining activation energies for these reactions remains a challenge.

The main challenge to modelling *ab-initio* electrochemical barriers in periodic simulation cells of feasible size is that the workfunction (often used as an alias for the electrode potential) changes by about 1-2 $eV^{12,13}$ during the course of a reaction involving an ion-electron pair or adsorption of a polar intermediate. This change is an artifact of the finite nature of a super cell, containing a fixed number of electrons. At the hypothetical infinitely sized cell there would be

no change in the workfunction accompanying a reaction, guaranteeing that the simulated electrochemical reaction proceeds without a change in the potential.^{11,12,14}

In the past decade, a variety of methods to address this challenge have been developed.^{11,12,14–25} These methods can be broadly grouped into two categories, extrapolation and grand-canonical schemes. Extrapolation methods seek to determine activation energies at the limit of infinite cell size by correcting DFT energies for finite cell size effects. For example, in Ref 11, 12 the infinite cell limit is reached by extrapolating energies from DFT calculations done at successively larger cell sizes, through so-called cell extrapolation. Another approach is to a priori assume that the electrochemical interface can be modelled as a parallel plate capacitor, ^{2,14,16} where the periodically repeated ion (or adsorbate) forms one end and the metal surface the other. The charge stored in the parallel plate capacitor is determined through a charge partitioning approach and the potential is estimated through the workfunction. In this "charge extrapolation" scheme the DFT energies are corrected with a purely electrostatic model, to obtain energies at the infinite cell size, assuming a linear change in potential with the amount of charge on the capacitor plates. Alternatively, grand-canonical (GC) methods keep the workfunction constant by adding or subtracting excess electrons within the simulation cell, along with a corresponding countercharge in different possible continuum models of the electrolyte.^{15,18,23,26–32} Recently, a class of methods have attempted to combine the two approaches, i.e. performing DFT calculations which change the workfunction by adding or subtracting excess electrons while using the capacitor equations to interpret the obtained energies. ^{13,22}

In theory, it has been shown that both GC and extrapolation methodologies are equivalent in specific limiting cases, such as adsorption reactions of polar species. For example, Ref 17 showed that for $CO_2 \rightarrow CO_2^*$ both GC and extrapolation procedures provide the same potential dependent energies. However, in practice, challenges still remain. Cell extrapolation is computationally demanding, while charge extrapolation necessitates charge partitioning, which has short-comings in cases of strong hybridisation between atoms. For example, charge transferred along the reaction path for protonation to oxygen and nitrogen intermediates show sharp changes, inconsistent with a capacitor treatment. This behaviour is likely a failure of charge partitioning as a consequence of increasing hybridisation between the reacting species.³³ Furthermore, rotation of water along a reaction path leads to abrupt changes in the workfunction. Grand-canonical methods require an accurate capacitance in order to avoid cell-size dependence of reaction energetics.¹³ Finally, all of the above methods are typically applied with static water structures, while dynamic simulations under constant potential are only recently emerging.^{34,35}

In this work, we propose a method to determine potential dependent energetics of electrochemical reactions by building upon the framework of extrapolation methodologies. The strength of our approach is that we determine the charge transfer coefficient directly from atomic positions and atom centered forces, without the need for explicit partitioning of the charge density or performing multiple DFT calculations. We begin by illustrating the current extrapolation based procedure to determine charge transfer coefficients and potential dependent energies for a prototype reaction of a proton-electron transfer to C adsorbed on Pt(111). We then develop a model which relates the atom centered forces to the charge transfer coefficient. The computational overhead associated with implementing our approach is equivalent to a typical finite difference Hessian calculation. We show that the force-based method is able to provide consistent charge transfer coefficients for a range of reactions, irrespective of how strongly the reacting species are hybridised. We benchmark this methodology against calculations done at different cell sizes, i.e. through cell extrapolation and discuss possible limitations.

Extrapolation using the capacitor model of the electrochemical interface

In this section, we review how to obtain the charge transfer coefficient and the potential dependent energies of an elementary reaction, based on the framework of extrapolating to the infinite cell size. As in previous work, ^{11–14,16} we assume that the electrochemical interface is represented by a capacitor of constant capacitance, C and is invariant with respect to the electrode potential and the reaction geometry.¹³ We expect this assumption to hold for small changes in potential far from the potential of zero charge (pzc) where water structures are relatively ordered.³⁶ In such a purely electrostatic view of the electrochemical interface, a redox reaction, such as protonation, would be equivalent to altering the charge stored in this capacitor.

By treating the metal-water interface from our DFT computations as a parallel plate capacitor, we explicitly determine the different energy contributions associated with a reaction. We write the energies of a given state (corresponding to a particular number of atoms and geometry) E, as a function of the charge stored in the capacitor q in the form of a Taylor series expansion,^{13,21}

$$E = E_0 + q \frac{\partial E}{\partial q}|_{q=0} + \frac{q^2}{2} \frac{d^2 E}{dq^2}|_{q=0} + \mathcal{O}\left(q^3\right), \ (1)$$

$$E = E_0 + q\phi_0 + \frac{q^2}{2C},$$
 (2)

where E_0 corresponds to a purely chemical, non-electrostatic energy, $\partial E/\partial q$, the first derivative of energy with charge, corresponds to the workfunction at q = 0, ϕ_0 , and the second derivative of energy with q corresponds to the inverse of the capacitance, 1/C. To account for reaction energies, we calculate the energy to go from state 1 to state 2, $\Delta E_{1\rightarrow 2}$. This term corresponds to the reaction energy from a DFT calculation (the *y*-axis of either plot in Figure 1). Taking the difference between single state energies for 1 and 2 from Equation 2 gives,

$$\Delta E_{1\to 2} = \Delta E_0 + (q_2 - q_1) \phi_0 + \frac{1}{2C} \left(q_2^2 - q_1^2 \right),$$
(3)

which can be simplified using the parallel-plate capacitor relationship $C = q_2/(\phi_2 - \phi_0) = q_1/(\phi_1 - \phi_0)$

$$\Delta E_{1\to 2} = \Delta E_0 + (q_2 - q_1) \left[\frac{\phi_1 + \phi_2}{2} \right]$$
 (4)

Note that, as described in Ref 17, we can write the infinite cell size energy, ΔE_{∞} in the limit that the potential does not change during the reaction, i.e. $\phi_1 = \phi_2 = \phi$ as,

$$\Delta E_{\infty} = \Delta E_0 + (q_2 - q_1)\phi \tag{5}$$

Comparing Equation 4 and Equation 5, $\Delta E_{\infty} = \Delta E_{1 \rightarrow 2}$ when $\phi = (\phi_1 + \phi_2)/2$.

Figure 1 shows $\Delta E_{1\rightarrow 2}$ for two reaction steps, initial state (IS) to final state (FS), $\Delta E_{IS\rightarrow FS}$ and transition state (TS) to final state (FS), $\Delta E_{TS\rightarrow FS}$. As we primarily study *acidic* reactions in this work, we perform DFT calculations in different cell sizes with varying the hydrogen atom concentration in the water layer in the IS. These hydrogen atoms spontaneously donate their electron to the electrode, changing the electrode potential, and become protons.³⁷ The greater the number of protons per unit area, the lower the overall potential.

The slopes of the lines in Figure 1(a,b) correspond to differences in charges stored in the capacitor, $q_{\text{TS}\rightarrow\text{FS}} = 0.37e$ and $q_{\text{IS}\rightarrow\text{FS}} = 0.74e$. Physically, $q_{\text{TS}\rightarrow\text{FS}}$ represents the charge transferred from the water layer to the metal going from TS to FS. Thus, Equation 4 allows for a clear determination of the charge transfer coefficient from DFT energies and workfunctions. Note that $q_{\text{IS}\rightarrow\text{FS}} \neq 1$, which is in line with previous findings.^{10,14-16} This lower than expected value of the charge transfer coefficient is likely caused by hybridisation of the metal with the proton in the IS.³⁸

To summarise, there are three critical quantities to obtain potential dependent energies from DFT calculations, as seen from Equation 4. Two of these quantities, the reaction energy



Figure 1: Variation of a) reaction energies b) barriers for $C + H^+ + e^- \rightarrow CH$ with the mean workfunction. Atomic positions of the initial state and the transition state are shown within insets; the reacting proton is marked in blue. Colors indicate different cell sizes with different proton concentrations. Cell sizes annotated with a ' indicate multiple protons in the unit cell; the rest have a single proton in the unit cell.

 $\Delta E_{1\rightarrow 2}$ and the mean workfunction $(\phi_1 + \phi_2)/2$ are outputs of DFT calculations performed in a single cell size. The charge transfer coefficient, $(q_2 - q_1)$, however, requires DFT calculations in several different proton concentrations / cell sizes or the use of charge partitioning schemes.

Force based method for obtaining charge transfer coefficients

In this section we develop a model to obtain the charge transfer coefficient, $q_2 - q_1$, from a handful of DFT calculations, without the need for performing computations at multiple cell-sizes. We start by defining a normalised reaction coordinate between two states, $\boldsymbol{\omega}$, a reaction length l_e and the reaction coordinate \boldsymbol{Q} (bold symbols denote vectors; standard typeface indicates norm of the vectors). These three quantities are related as,



Figure 2: Schematic showing the normalised reaction path for a proton electron transfer reaction, $C + H^* + e^- \rightarrow CH^*$ on a metal surface. ω denotes the idealised reaction path; IS, TS and FS are the initial, transition and final state respectively.

$$\boldsymbol{Q} = l_e \boldsymbol{\omega} \tag{6}$$

Figure 2 shows a schematic of the reaction, $H^+ + e^- + C^* \rightarrow CH^*$, where we have marked ω as it changes from the IS through the TS to the FS. Throughout this work, we define the TS as the state corresponding to the energy maximum along a reaction path (see Methods section in the SI). In the IS, the reacting proton is bound to H₂O forming a hydronium ion. As the reaction proceeds, the O–H bond is stretched until reaching the TS, followed by a reduction in of the C–H bond length until reaching the FS. Within this picture, ω is 0 at the IS, 1 at the FS and any value in between 0 and 1 at the TS.

To begin, we illustrate the reaction coordinate consisting of moving just the proton (shown in cyan in Figure 2) to the surface. We will later generalise this coordinate to any number of atoms. We Taylor expand \boldsymbol{q} , which is the variation of the vector containing the charge transfer components along $\boldsymbol{\omega}$. In general, between two states 1 and 2, where $\boldsymbol{\omega} = 0$ at state 1 and $\boldsymbol{\omega} = 1$ at state 2, for each dimension,

$$\boldsymbol{q}_{2} = \boldsymbol{q}_{1} + \left(\frac{d\boldsymbol{q}}{d\boldsymbol{\omega}} \bigg|_{\boldsymbol{\omega}=0} \boldsymbol{\omega} \right) + \mathcal{O}\left(\boldsymbol{\omega}^{2} \right) \qquad (7)$$

The quantity in the brackets in Equation 7 is rewritten as a function of the dipole moment measured along the corresponding dimension, μ , and Q by realising that the poles of the dipole are at a distance l_e such that,

$$\boldsymbol{\mu} = l_e \boldsymbol{q} \tag{8}$$

leading to,

$$\frac{d\boldsymbol{q}}{d\boldsymbol{\omega}} = \frac{d\boldsymbol{\mu}}{d\boldsymbol{Q}} \tag{9}$$

Note that in the limit of $l_e \to 0$, $\mu \to 0$ such that q is always finite.

In typical periodic surface computational setups, $\boldsymbol{\mu}$ for a given computational cell may be determined by integrating the charge density $\boldsymbol{\rho}$, as $\boldsymbol{\mu} = \int \boldsymbol{\rho} \boldsymbol{r} d\boldsymbol{R}$ where \boldsymbol{R} are the Cartesian coordinates and \boldsymbol{r} is a running index along an axis. Additionally, most modern *ab-initio* codes provide $\boldsymbol{\mu}$ as an output.

Finally, we obtain the quantity $d\mu/dQ$ by

finding the dipole derivative along R and then projecting onto the reaction mode ω (represented in Cartesian coordinates), identical to Ref 39.

$$\frac{d\boldsymbol{\mu}}{d\boldsymbol{Q}} = \frac{d\boldsymbol{\mu}}{d\boldsymbol{R}} \cdot \boldsymbol{\omega} \tag{10}$$

where μ is the dipole moment vector in Cartesian coordinates. Finally, Equation 10 can be generalised to include any number of atoms by writing the dot product of the right-hand side as a sum over *i* atoms,

$$\frac{d\boldsymbol{\mu}}{d\boldsymbol{Q}} = \sum_{i=1}^{N} \frac{d\boldsymbol{\mu}}{d\boldsymbol{R}_{i}} \cdot \boldsymbol{\omega}_{i}, \qquad (11)$$

where N is the number of atoms involved in the reaction. Note that N does not have to be all atoms in the unit cell, but the relevant atoms can be chosen as the one participating in the reaction. Following Equation 11, the overall equation for the differences in charges between two states 1 and 2 from Equation 7 reduces to,

$$\boldsymbol{q}_2 - \boldsymbol{q}_1 = \sum_{i=1}^N \frac{d\boldsymbol{\mu}}{d\boldsymbol{R}_i} \cdot \boldsymbol{\omega}_i$$
 (12)

where, $q_2 - q_1 = |\boldsymbol{q}_2 - \boldsymbol{q}_1|$ is the charge transfer coefficient.

As a final simplification of the model, we will henceforth refer to $d\mu/dR$, as the derivative of μ along the direction of the surface normal, as electrochemical barriers are conventionally computed in quasi-2D surface setups, where we are usually concerned with the dipole moment only in the out-of-plane direction.²

We obtain the dipole derivative in two ways, similar to Ref 39.

1. Moving atoms by small displacements ΔR , in the Cartesian coordinates R and then computing the derivative through finite differences

$$\frac{d\mu}{dR} = \frac{\mu^{j+1} - \mu^{j-1}}{2\Delta R}$$
(13)

where we have dropped the subscript (1,2 in Equation 12) on μ , since this finite difference operation is valid at any state. μ^{j+1} is the dipole moment at $+\Delta R$ and μ^{j-1} is the dipole moment at $-\Delta R$ from the equilibrium positions. We also explicitly denote the derivative with respect to R as $d\mu/dR$ (i.e. without the boldface typography).

2. Making use of the following equivalence between the dipole derivative and the first derivative of the force, F, with respect to the applied field, ξ (through, for example, a saw-tooth potential), and using $\mu = dE/d\xi$ and F = dE/dR,

$$\frac{d\mu}{dR} = \frac{d}{d\xi}\frac{dE}{dR} = \frac{dF}{d\xi} \tag{14}$$

We compute the force based derivative through finite differences by applying saw-tooth potentials of different magnitude with a spacing of $\Delta \xi$

$$\frac{dF}{d\xi} = \frac{-F^{j+2} + 8F^{j+1} - 8F^{j-1} + F^{j-2}}{12\Delta\xi}$$
(15)

where we use a four point finite difference stencil of ξ to reduce the requirements for accurate forces from the SCF cycle. Two point-stencils may be used, while paying special attention to the convergence of the atom centered forces (see SI). Superscripts of F denote the order of the applied field, such that F^{j+2} are the forces at $\xi + 2\Delta\xi$, F^{j+1} are the forces at $\xi + \Delta\xi$ and so on.

In practice, we obtain ω_i by simply normalising the atomic positions of state 1 and 2,

$$\omega_i \approx \frac{\text{positions}_{i,2} - \text{positions}_{i,1}}{|\text{positions}_{i,2} - \text{positions}_{i,1}|}$$
(16)

Finally, the differences in charge stored between two states 1 and 2 is obtained by substituting Equation 14 into Equation 12,

$$q_2 - q_1 = \sum_{i=1}^{N} \left(\frac{dF}{d\xi_i} \cdot \omega_i \right)_i \tag{17}$$

Figure 3 shows that obtaining the derivatives from either displacement through dipole



Figure 3: Equivalence of the dipole derivative $d\mu/dR$ and the force derivative $dF/d\xi$ for a range of elementary electrode reactions. Mean absolute error between $dF/d\xi$ and $d\mu/dR$ is 0.002 e

(Equation 14) or through forces (Equation 15) is equivalent. Thus, the application of Method 2 is more appealing as it only relies on the atom centered forces from a DFT-calculation at a chosen structure (as in $dF/d\xi$) instead of atomic displacements (as in $d\mu/dR$). Note that this equivalence is only seen when the forces are properly converged; tests for different convergence criteria are shown in SI Note 1. Note that this method, combined with the extrapolation procedure in Equation 4, provides a direct way to determine potential dependent electrochemical barriers by using just the outputs of a DFT calculation along with the transition state structures, without the need for any a priori assumptions to its value. 16,22

Application to electrocatalytic reactions

In this section, we apply the force-based methodology to several electrochemical reactions, including protonation and adsorption of polar intermediates. We compare the value of the transfer coefficient, $q = (q_2 - q_1)$ from Equation 17 with that obtained by fitting multiple cell sizes through Equation 4.

We start by investigating the prototype reaction discussed in Figure 1, i.e. $H^+ + e^- + C^* \rightarrow$ CH^{*}. Figure 4a shows the variation of the energy and Figure 4b (points) shows q (Equation



Figure 4: a) Raw energies from images used in a nudged-elastic band calculation of $C^* + H^+ + e^- \rightarrow CH^*$ b) (points) $(q_2 - q_1)$, where q_2 refers to FS and q_1 to the IS, obtained for all images for the reaction $H^+ + e^- + C^* \rightarrow CH^*$ (lines) erfc fit to show the change in charge along reaction path c) Energy vs. mean potential based on fitting (black line) and the predictions from finite difference for different cells (colors)

17) along the reaction path. We consider just the proton and the adsorbed C atom in the summation of Equation 17. q goes through a maximum at the TS falling to zero when the CH^{*} species is formed, mirroring the change in energy with reaction path. Different proton concentrations, spanning a potential range of 2 V in potential, are consistent in their force-based prediction of $q \approx 0.3e$, which is similar to the value of q = 0.37e from fitting over the varying cell sizes in Figure 1.

In contrast to the slope in Figure 1, the predicted q is much lower in the case of the IS (first point in Figure 4b). The reason for this lower prediction is that in the IS the reacting proton does not exist as a single entity. Rather the charge is spread out over the hydronium ion (top right inset Figure 4b). This spreading out of the charge explains why the predicted q for a single proton is roughly $\frac{1}{3}$ rd that determined in Figure 1a. If the charge transfer coefficient for IS \rightarrow FS is required, a simple reaction coordinate of $\omega = (0, 0, 1)$ may be chosen and the contribution for each equivalent proton may be considered. To represent such a situation, we represent $q_{\rm IS}$, $q_{\rm TS}$ and $q_{\rm FS}$ as a complementary error function (solid lines in Figure 4b). With

this approach, $q_{\rm IS \rightarrow FS} \approx 0.6 - 0.75$ e, which is in line with Figure 1a.

The central quantity of interest for the purposes of reaction kinetics studies is the charge transfer coefficient, i.e. q at the TS with respect to a thermodynamically stable state (such as IS or FS). Specifically, the variation of the TS energy with potential is typically an input into micro-kinetic mechanic models. Figure 4c shows the variation of ΔE^{TS} with the mean potential, $(\phi_{\rm TS} + \phi_{\rm FS})/2$ for different cell sizes (and hence different proton concentrations). The black line indicates the least squares fit to the cell sizes and lines of other colours indicate the predicted variation of the ΔE^{TS} through the q obtained in Figure 4c. Thus, for transition states, the force-based method is able to predict the variation of energies with potential.

We now compare the charge transfer coefficient for our force-based method with the cell extrapolated value for a few prototype electrochemical reactions. To do so, we perform electrochemical barrier calculations for three reactions, $C^* + H^+ + e^- \rightarrow CH^*$ (this work), $OH^* + H^+ + e^- \rightarrow H_2O$ and $H^* + H^+ + e^- \rightarrow H_2$ (from Ref 14, 16). Figure 5 shows a parity plot between the q obtained from Equation 17 and



Figure 5: Parity plot for q from fitting through Equation 4 for a series of increasingly larger unit cells and through the force-based method as in Equation 17; dashed line indicates exact fit and green band indicates ± 0.1 error with either methodology. Alternative ω denotes an idealised reaction path where the proton descends directly to the surface along the direction of the surface normal.

from fitting (Equation 4), the dashed line indicates an exact match. For these three reactions, the obtained values for both methods are within $\pm 0.1e$ for all cells.

As in Ref 17, we suggest that adsorption processes can be considered within the framework of the capacitor model. While an *ab-initio* reaction path would be missing, we choose a simplified reaction path, where all atoms participating in the reaction move simultaneously along the axis perpendicular to the surface. For example, in the case of the CO_2 adsorption reaction, ω would correspond to a transition from a bent CO_2^* molecule to a linear CO_2 . Figure 5 shows that this approximation leads to qwhich is slightly underestimated from the corresponding value obtained by fitting, likely a consequence of assuming an idealised reaction path.

In the case of IS \rightarrow FS reaction paths, such as in H⁺+e⁻ \rightarrow H^{*}, we again see the that the predicted q from finite differences is roughly a third of the value predicted by fitting (due to the hybridised nature of the proton in the IS). An idealised reaction coordinate $\omega = (0, 0, 1)$ corresponding to a proton dropping linearly along the surface-normal axis, leads to a closer match between the two methodologies (denoted as alternative ω in Figure 5).

Potential issues to the application of this force-based method include rotation of water during nudged-elastic band calculations, leading to changes in workfunctions that do not represent those coming from the reaction. Inaccuracies in forces determined through the DFT self-consistent cycle also lead to noise in the finite difference computation.

The overall strength of our methodology is its ability to determine the charge transfer coefficient, using a simple model of the interface, without the need for computationally expensive multiple cell size computations or methodological extensions to standard DFT setups. Besides treating ion-electron transfers, it can also be used to determine the electrode potential dependence of polar adsorbates like CO_2^* . Given its ability to determine potential dependence of electrochemical reactions at modest computational expense, we envision its use in developing micro-kinetic models to understand electrochemical mechanisms.^{33,40}

Conclusions

Activation energies are critical to a mechanistic understanding of electrochemical reaction processes. However, significant challenges such as cell-size dependence pose a challenge to determining accurate *ab-initio* electrochemical barriers. In this work, we suggest a simple model to compute the charge transfer coefficients, and hence the activation energies, with just a single DFT calculation. Our method builds upon previous extrapolation procedures and removes the short-comings of explicit partitioning of the charge density, which give rise to ambiguous or unphysical jumps in charge transfer along the reaction pathway. We show that the charge transfer coefficient is related to the derivative of the atom centered forces with respect to applied field. We perform a series of electrochemical barrier calculations and show that the charge transfer coefficient computed with our method is in good agreement with the value obtained by

performing traditional cell-extrapolation procedures, which require multiple cell sizes. We show that our methodology can be successfully used for transition states as well as polar adsorbates, both critical species in electrochemical reactions.

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Supporting Information Available

The following files are available free of charge.

• SI: Supporting information

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