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Practical Considerations for Continuum Models Applied to Surface Electrochemistry

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Charge density isosurface illustrating the strong dipole moment exhibited by CO₂ on Pt (111). The yellow surface corresponds to electron density equal to $0.01 \text{ e } \text{\AA}^{-3}$, while blue corresponds to negative electron density of the same magnitude. The strong dipole moment gives a potential dependence of CO₂ adsorption, despite no formal proton/electron transfer process occurring. These potential dependencies can be seen with continuum solvation techniques, which we explore in this work.

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1 Abstract

Modelling the electrolyte at the electrochemical interface remains a major challenge in *ab initio* simulations of charge transfer processes at surfaces. Recently, the development of hybrid polarizable continuum models/*ab initio* models have allowed for the treatment of solvation and electrolyte charge in a computationally efficient way. However, challenges remain in its application. Recent literature has reported that large cell heights are required to reach convergence, which presents a serious computational cost. Furthermore, calculations of reaction energetics require costly iterations to tune the surface charge to the desired potential. In this work, we present a simple capacitor model of the interface that illuminates how to circumvent both of these challenges. We derive a correction to the energy for finite cell heights to obtain the large cell energies at no additional computational expense. We furthermore demonstrate that the reaction energetics determined at constant charge are easily mapped to those at constant potential, which eliminates the need to apply iterative schemes to tune the system to a constant potential. These developments together represent more than an order of magnitude reduction of the computational overhead required for the application of polarizable continuum models to surface electrochemistry.

2 Introduction

In the past decade, advances in density functional theory (DFT) has paved the way for the theoretical mechanistic study of electrochemical processes. The computational hydrogen electrode (CHE) model [1], in particular, has provided an elegant way to study coupled ion-electron transfer reactions without explicitly modeling charged species. However, the calculation of reaction barriers and the associated kinetics requires the treatment of electrolyte at the interface. To this end, a great deal of effort has been invested to effectively treat charged species at the interface using DFT, ranging from a variety of continuum approximations [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17] to a fully *ab initio* approach.[18, 19, 20, 21, 22]

Modeling the electrochemical interface with either a continuum electrolyte or with a fully *ab initio* electrolyte come with their own benefits and challenges.[23] In principle, one of the primary benefits of using a continuum approach is the lack of simulation cell size dependence on the reaction energetics, since the interface can be set to a given potential by modifying the surface charge density. This is not the case in fully *ab initio* simulations, since the potential changes across the reaction coordinate, proportional to the simulation cell size.[18, 19] However, several recent reports on hybrid continuum/*ab initio* approaches [24, 25, 26, 27, 23] have noted that excessively large simulation cells are required to reach convergence, which was attributed to the slow decay of the electrostatic potential in the direction normal to the surface. Furthermore, the iterative scheme to charge the surface to a desired potential can dramatically increase the cost of a calculation.[28, 23] In this article, we present a capacitor

model for the relationship between the reaction energetics and the potential and charge. From this model, we derive a simple correction that relates the energetics determined at small to those at large cells at no additional computational cost. We furthermore demonstrate that the iterative scheme to charge the surface to a given potential is unnecessary, since the energetics at constant charge are trivially mapped to those at constant potential. Combined, these two developments allow for more than an order of magnitude reduction in computational cost required in the determination of electrochemical reaction energetics with hybrid continuum/*ab initio* models.

3 Methods

This work uses the Vienna ab-initio Software Package[29, 30, 31] in conjunction with VASPsol.[11, 32] Core electrons were modeled with projector augmented wave pseudopotentials, [33] while valence electrons were expanded as plane-waves up to a kinetic energy cutoff of 500 eV. When optimizing bulk platinum to determine the appropriate lattice constant, the Brillouin zone was sampled with a $12 \times 12 \times 12$ γ -centered Monkhorst-Pack[34] k-point mesh. The optimized lattice constant was determined to be 3.990 Å. Exchange and correlation interactions were accounted for using the RPBE functional.[35] A 2×2 supercell of Pt (111) was used as the model system. 4 layers were used in a symmetric unit cell, with the middle two layers fixed and the outer two free to relax.

Geometries were considered optimized when the maximum force on any unconstrained atom in the system was below $0.03 \text{ eV } \text{\AA}^{-1}$. 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.

VASPsol treats the electrolyte at the electrochemical interface as a polarizable continuum. To ensure overall charge neutrality, it places counter-charge via the linearized Poisson-Boltzmann (LPB) equation. We chose a Debye length of 3 Å, which corresponds to a bulk electrolyte concentration of 1M. Details regarding the implementation of this solvation model can be found in its documentation.[32, 11]

4 Results and Discussion

We formulate a simple capacitor model that describes the charging response of surfaces undergoing elementary chemical and electrochemical processes. This simple model shows that, where the capacitance is constant and invariant amongst the states considered, the potential dependence of these elementary processes arises only from the potential of zero charge and capacitance of the surface. We show that the model can be used to correct for the large vacuum required as noted in previous literature, allowing for slab separations comparable to those in vacuum calculations. This correction is essentially due to a potential shift, similar to those derived in previous works.[36, 37] Finally, we apply the model

to show that the energy difference at constant charge corresponds to the grand canonical free-energy difference at the average potential of the states considered.

4.1 Formulation of the Model

In this section we formulate the Taylor expansion of the energy, which expresses it as a function of surface charging properties, the potential of zero charge and the capacitance. We will first consider charging the interface for a given surface state and then consider the energy difference between two states (i.e. representing, for example, reaction or activation energies) under conditions of both constant charge and constant potential.

4.1.1 For a Single State

The Taylor expansion of energy as a function of the excess surface charge, q , is

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

The first order term is the energy required to bring a unit charge into the slab at zero charge from a specific reference energy level,

$$\left. \frac{\partial E}{\partial q} \right|_{q=0} = -\mu_{e,0} = \Phi_0 - \Phi_{\text{vac}} \quad (2)$$

where $\mu_{e,0}$ is the Fermi level, which in VASP is calculated relative to the average self-consistent potential. The internal reference level in VASP is different from the bulk electrolyte which is an appropriate electrochemical reference. We therefore express $-\mu_{e,0}$ by two terms: the work function at zero charge relative to the bulk electrolyte potential, Φ_0 , and the shift between the electrolyte potential and the zero potential reference, Φ_{vac} , as illustrated in Figure 1. Φ_{vac} is printed in VASPsol as the negative of the output flag `FERMI_SHIFT` and decreases as a function of cell height. Figure 1 also shows that the electrolyte potential is already flat at typical cell sizes, and so the slow convergence of energies with respect to cell height [24, 25, 26, 27, 23] arises solely from variations in Φ_{vac} rather than a slow decay of countercharge density in the continuum electrolyte.[26]

In a charged LPB system, the absolute value of the potential is fixed even in the presence of periodic boundary conditions due to the additional ionic screening term in the Poisson equation. However, for a finite cell size, the value of the potential in the bulk electrolyte is non-zero and depends on the excess charge, due to the choice of reference potential in VASP. This results in a non-zero boundary integral term to the electrostatic free energy and a constant shift of the potential that corresponds to charge times the potential shift. As we show below, by subtracting out the contribution of Φ_{vac} , converged energies can be readily obtained from cell heights comparable to those used in vacuum calculations. In principle this reference mismatch arises in any plane-wave DFT code

Figure 1: Illustration of the different potential levels in VASPsol using the example of adsorbed CO₂ on Pt(111).

that uses periodic boundary conditions in all three dimensions. For example, in Quantum Espresso's[38] polarizable continuum model Environ[39], an analogous quantity is printed as the shift due to the parabolic periodic boundary condition correction.

The second derivative in the Taylor expansion can be expressed as a function of the capacitance C , which we assume to be constant with q :

$$\left. \frac{\partial^2 E}{\partial q^2} \right|_{q=0} = \left. \frac{\partial \Phi_0}{\partial q} \right|_{q=0} = \frac{1}{C} \quad . \quad (3)$$

The energy as a function of surface charge is therefore

$$E(q) = E(q=0) + q(\Phi_0 - \Phi_{\text{vac}}) + \frac{1}{2C}q^2 \quad . \quad (4)$$

This is the expression given by previous works [40, 6, 41, 42, 25] with the exception of the nonzero electrolyte level correction, Φ_{vac} .

Reaction energetics are generally considered as a function of potential. From $q = C(\Phi - \Phi_0)$ and taking the limit $\Phi_{\text{vac}} \rightarrow 0$,

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

Here the subscript ∞ refers to the quantity in the limit of infinite cell height, i.e. in the limit $\Phi_{\text{vac}} \rightarrow 0$. As in previous works,[28, 23] we obtain the grand canonical free-energy of the system by incorporating the exchange of energy from an external electron reservoir:

$$\Omega_{\infty}(\Phi) = E(\Phi) - q\Phi = E(\Phi) - C\Phi(\Phi - \Phi_0) \quad . \quad (6)$$

Here q as before represents the system charge, and Φ is the system potential (equivalent to the chemical potential of the electron reservoir).

4.1.2 For the Difference Between Two States

Under a constant charge q and in the limit of $\Phi_{\text{vac}} \rightarrow 0$, the energy difference between two states are

$$\Delta E_{\infty}(q) = E_2(q) - E_1(q) \quad (7)$$

$$= \Delta E(q=0) + \Delta(q\Phi_0) + \frac{\Delta q^2}{2C} \quad (8)$$

$$= \Delta E(q=0) + q\Delta\Phi_0 \quad . \quad (9)$$

Equivalently, we can write the energy difference between these states at constant potential:

$$\begin{aligned} \Delta E_{\infty}(\Phi) &= E_2(\Phi) - E_1(\Phi) \\ &= \Delta E(\Phi = \Phi_0) - \frac{C}{2} \Delta\Phi_0^2 \\ &= \Delta E(q=0) - C\bar{\Phi}_0\Delta\Phi_0 \quad . \end{aligned} \quad (10)$$

In the last step, we further introduced the average PZC between the initial and final state, $\bar{\Phi}_0$, via the identity $\frac{1}{2}\Delta\Phi_0^2 = \bar{\Phi}_0\Delta\Phi_0$.

Lastly, we can examine the change in grand canonical free-energy at constant potential and in the limit of $\Phi_{\text{vac}} \rightarrow 0$, between the two states as in (6):

$$\begin{aligned} \Delta\Omega_{\infty}(\Phi) &= \Delta E(\Phi) - \Delta(q\Phi) \\ &= \Delta E(\Phi = \Phi_0) + C\Delta\Phi_0(\Phi - \bar{\Phi}_0) \end{aligned} \quad (11)$$

where we used the capacitor equation in the constant potential limit $\Delta q = -C\Delta\Phi_0$.

To illustrate the validity of the model, we use the simple example of CO_2 adsorption on Pt(111). This involves the creation of a strong dipole moment, as is shown in the top panel of Figure 2. Here, the charge density isosurface is calculated as

$$\rho_{\text{diff}} = \rho_{\text{total}} - \rho_{\text{slab}} - \rho_{\text{CO}_2} \quad . \quad (12)$$

The bottom panel shows the agreement between the model and the DFT simulation. We calculate the binding energy of CO_2 as

$$\Delta E_{\text{CO}_2} = \frac{1}{2} (E_{*\text{CO}_2} - E_* - 2E_{\text{CO}_2(\text{g})}) \quad . \quad (13)$$

In this equation, ΔE_{CO_2} is the binding energy of CO_2 , $E_{*\text{CO}_2}$ is the energy of the system of the slab with two CO_2 molecules adsorbed (i.e. due to the

symmetry in the z -direction, as illustrated in Figure 1) at a given potential, E_* is the energy of the clean slab at the same potential, and $E_{\text{CO}_2(\text{g})}$ is the energy of a gas-phase CO_2 molecule. In the bottom panel of Figure 2, the points represent the calculated change in grand canonical free-energy associated with CO_2 adsorption as obtained from Eq. 6 and Eq. 13 while the line represents the model given in Equation 11. The points have been corrected to achieve the limit $\Phi_{\text{vac}} \rightarrow 0$ (which the model, Eq. 11, assumes), demonstrated in the next section. Φ_0 and $E(\Phi = \Phi_0)$ from the model were determined directly from $\mu_{\text{e},0}$ and Φ_{vac} , while C was determined by a linear fit of $q(\Phi)$, illustrated in SI Note 1. We find the capacitance of the clean Pt (111) surface to be $12.6 \mu\text{F cm}^{-2}$, and the capacitance with CO_2 adsorbed in a (2x2) supercell of Pt (111) to be $10.1 \mu\text{F cm}^{-2}$. This small change in capacitance contributes to the slight non-linearity observed in the bottom panel of Figure 2. We note that in larger cell sizes, this change in capacitance decays quite rapidly. In a (4x4) supercell, the capacitance decreases by only $0.1 \mu\text{F cm}^{-2}$. Since the quadratic term is proportional to the change in capacitance, we therefore find the assumption of constant capacitance between states to be quite robust to the addition of adsorbates.

Figure 2: Demonstration of the simple model in describing the electrostatic response of Pt (111) to the adsorption of CO_2 . Top: Charge density difference isosurface demonstrating the strong dipole moment created by CO_2 at the surface. Yellow corresponds to an isosurface of positive electron density equal to $0.01 \text{ e } \text{\AA}^{-3}$, while blue corresponds to a negative electron density of $0.01 \text{ e } \text{\AA}^{-3}$. Bottom: Agreement between the derived model and the associated DFT calculations. Here points illustrate calculated binding energies from DFT, and the dashed line corresponds to the model derived in Eq. 6.

4.2 Correcting for Finite Separation Between Periodic Images

In what follows, we show the corrections needed to obtain the energy associated with a zero potential reference in bulk electrolyte using finite cell heights.

4.2.1 Correction at Constant Charge

We consider again Eq. (9), which was derived in the limit of infinite cell height, i.e. $\Phi_{\text{vac}} \rightarrow 0$. If we neglect to make this assumption and isolate the terms that depend on Φ_{vac} , we see:

$$\Delta E(q) = \Delta E(q=0) + q\Delta(\Phi_0) - q\Delta(\Phi_{\text{vac}}) \quad . \quad (14)$$

In the limit of infinite separation of the surface slabs, the potential in the electrolyte region $\Phi_{\text{vac}} \rightarrow 0$, and therefore also $\Delta\Phi_{\text{vac}} \rightarrow 0$ and $\mu_{\text{e},0} \rightarrow -\Phi_0$. We can then write for the extrapolated energy difference at infinite separation of the slabs

$$\Delta E_{\infty}(q) = \Delta E(q) + q\Delta\Phi_{\text{vac}} \quad . \quad (15)$$

Here $\Delta E_{\infty}(q)$ is the change in energy between two states at constant charge in the limit of an infinite separation between periodic slabs, $\Delta E(q)$ is the difference in energy with finite separation.

To demonstrate this, we have calculated the binding energy of CO_2 on Pt (111) at a constant surface charge density of $6 \mu\text{C cm}^{-2}$ at varying amounts of separation between periodic images. Figure 3a shows the agreement between the corrected energy and the large vacuum limit, while Figure 3b shows the decay of Φ_{vac} with separation distance.

Figure 3: Illustration of correction for finite separation between periodic slabs for a calculation at constant charge and constant potential. (a) The convergence of the corrected and uncorrected energy for large separations between periodic images at a constant surface charge of $6 \mu\text{C cm}^{-2}$. (b) The decay of the electrolyte potential, as it goes to zero in the limit of infinite separation between periodic images. (c) The convergence of the corrected and uncorrected constant potential grand canonical free-energy difference for large separations between periodic images. (d) The extrapolation of the energy difference to infinite cell size.

4.2.2 Correction at Constant Potential

Constant potential calculations, which are performed with the initial and final state at different charges such that the resultant potential remains the same, are of particular interest since they reflect experimental conditions. Beginning with (11) without taking the limit $\Phi_{\text{vac}} \rightarrow 0$, we see at constant potential:

$$\begin{aligned}\Delta\Omega(\Phi) &= \Delta E(q=0) + C(\Delta(\Phi_0\Phi_{\text{vac}}) - \Phi\Delta\Phi_{\text{vac}}) + C\Delta\Phi_0(\Phi - \bar{\Phi}_0) \\ &= \Delta E(q=0) + C\Delta\Phi_0(\Phi - \bar{\Phi}_0) - \Delta(\Phi_{\text{vac}}C(\Phi - \bar{\Phi}_0)) \\ &= \Delta E(q=0) + C\Delta\Phi_0(\Phi - \bar{\Phi}_0) - \Delta(q\Phi_{\text{vac}})\end{aligned}\quad (16)$$

Using the same argument as in the case of constant charge, in the limit of infinite separation between periodic images, $\Phi_{\text{vac}} \rightarrow 0$ and so we have:

$$\Delta\Omega_{\infty}(\Phi) = \Delta\Omega(\Phi) + \Delta(q\Phi_{\text{vac}}) \quad . \quad (17)$$

Where, as before, $\Delta\Omega_{\infty}(\Phi)$ refers to the change in grand canonical free-energy in the limit of infinite separation between periodic images, $\Delta\Omega(\Phi)$ to the finite energy difference, q to the charge, and Φ_{vac} to the average electrostatic potential in the calculation. Note that both q and Φ_{vac} vary from initial to final state.

Figure 3c illustrates the efficiency of this correction. The correction is generally larger in magnitude for constant potential calculations because the charge is changing with each state. This charge is multiplied by the electrolyte region electrostatic potential in the correction, which can be quite large, 1-2 V, for small cell heights. Whereas in the case of constant charge, there is significant error cancellation because the charge only multiplies the difference in average electrostatic potential. Figure 3d illustrates an extrapolation based method to obtain the infinite cell change in grand canonical free-energy, as illustrated in Ref. numbers[24]. We note that the remaining small differences in intercept are likely due to the tolerance on the applied potential (± 0.02 V) when optimizing the excess surface charge.

Overall, by avoiding the extremely large vacuums reported in literature, calculation times can be substantially reduced. In our example system, this results in a 7-fold speed increase per scf-step between the largest and smallest systems tested. As noted previously, the energetic variation corrected for here is general to polarizable continuum models in plane-wave codes that do not use an open boundary condition normal to the surface. Some codes, for example the polarizable continuum code Environ[39] implemented in QUANTUM-ESPRESSO[38] automatically corrects for the energetic shift due to the nonzero electrolyte potential. However, as noted by the VASPsol Github page[32] which advises users to add this correction to energies, VASPsol does not automatically add this correction, resulting in energetic deviations in a significant portion of literature.

4.3 Mapping Energetics at Constant Charge to Constant Potential

We now demonstrate that, in the limit of $\Phi_{\text{vac}} \rightarrow 0$ and constant capacitance, the change in energy at constant charge corresponds to the change grand canonical free-energy at a constant potential corresponding to the average potential between the states considered.

We recall from Eq. (9), that at constant charge the expression for the change in energy becomes:

$$\Delta E_{\infty}(q) = \Delta E(q=0) + q\Delta\Phi_0 \quad . \quad (18)$$

To compare this with (11), we will evaluate at the average potential of the two states, 1 and 2. This can be done by rearranging:

$$\begin{aligned} q_1 = q_2 &= C(\Phi_1 - \Phi_{0,1}) = C(\Phi_2 - \Phi_{0,2}) \\ &= C(\bar{\Phi} - \bar{\Phi}_0) \quad . \end{aligned}$$

Here Φ_1 and Φ_2 refer to the potential in states 1 and 2 respectively, while $\Phi_{0,1}$ and $\Phi_{0,2}$ refer to the potential at zero charge in states 1 and 2 respectively.

Substituting this expression for q into (18), we see:

$$\Delta E_{\infty}(\bar{\Phi}) = \Delta E(q=0) + C\Delta\Phi_0(\bar{\Phi} - \bar{\Phi}_0) \quad . \quad (19)$$

Comparing this expression to (10), we see that if the capacitance is constant and $\Phi_{\text{vac}} \rightarrow 0$, the change in energy at constant charge is equal to the change in grand canonical free-energy at the average potential. This result agrees with the results derived via Legendre transformation in Ref. numbers[43], and is a more general result of that in Ref. numbers[44], where it was shown that the transition state at constant charge and potential were identical.

To demonstrate this equivalence, we have calculated the binding energy of CO₂ on Pt (111) at both constant charge and constant potential, shown in Figure 4.

Figure 4: Agreement of the change in binding energy of CO_2 on Pt (111) at constant charge and the change in binding grand canonical free-energy at constant potential.

The agreement between these two quantities represents a further reduction in computational time when applying continuum methods to surface electrochemistry at constant potential. The iterative procedure by which the potential is set to a desired value, achieved by optimizing the system charge, is a significant cost increase compared to a standard calculation, approximately a factor of two to three.[28, 23] Rather than calculate the grand canonical free-energy at a fixed potential, one can instead do the simpler calculation at constant charge. When evaluated at the average potential in conjunction with the corrections for finite cell height, this gives an identical relationship between energy and potential.

5 Conclusions

In summary, we have presented a simple model for reaction energetics determined from hybrid continuum/*ab initio* models of the electrochemical interface, derived from a Taylor expansion of the energy. With this model, we derived simple corrections that allow for the calculation of energy differences at reasonable separation between periodic images, comparable to those seen in vacuum calculations. We further use the model to illustrate that the grand canonical free-energy for a reaction process at constant potential is exactly equivalent to the energy difference at constant charge, when applied in conjunction with the finite cell height correction. These two developments together give rise to more

than an order of magnitude reduction in the computational overhead required to apply polarizable continuum models to surface electrochemistry investigations.

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