Constant inner potential DFT for modelling electrochemical systems under constant potential and bias

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Abstract

Electrochemical interfaces and reactions play a decisive role in *e.g.* clean energy conversion but understanding their complex chemistry remains an outstanding challenge. Constant potential or grand canonical ensemble (GCE) simulations are indispensable for unraveling the properties of electrochemical processes as a function of the electrode potential. Currently, constant electrode potential calculations at the density functional theory (DFT) level are carried out by fixing the Fermi level of the simulation cell. However, the Fermi level from DFT calculations does not always reflect the experimentally controlled electrode potential or describe the thermodynamic independent variable in GCE-DFT *i.e.* the electrochemical potential of an electron reservoir ($\tilde{\mu}_e^{bath}$). Here we develop and implement the constant inner potential (CIP) method as a more robust and general approach to GCE-DFT simulations of electrochemical systems under constant potential or bias conditions. The CIP is shown to directly control $\tilde{\mu}_e^{bath}$ making the method widely applicable in simulating electrochemical interfaces. We demonstrate that the CIP and Fermi level GCE-DFT approaches are equivalent for metallic electrodes and inner-sphere reactions. The CIP method is shown to be applicable in simulating also semiconductor electrodes, outer sphere reactions, and a biased two-electrode cell for which the Fermi level approach does not reflect the experimental electrode potential. Unlike the Fermi level method, CIP does not require any electronic structure information as only the inner potential is needed, which makes the approach more compatible with classical force field or machine learning potentials. The CIP approach emerges as a general GCE-DFT method to simulate (photo)electrochemical interfaces from first principles.

Keywords: grand canonical, outer-sphere reactions, constant potential, density functional theory, machine learning potential, electrochemistry, electrocatalysis, quantum transport

1 Introduction

Electrochemical systems and reactions are ubiquitous in modern energy conversion applications, electrosynthesis, and sensors. Essential to all electrochemical systems is the ability to control reaction thermodynamics and kinetics by the application of an electrode potential. While experiments are routinely performed under constant potential conditions and referenced against well-defined reference electrodes, realizing constant potential atomistic simulations has been very challenging.[1, 2]

In experiments, the potential of a working electrode is controlled from the backside of the electrode through connections to an external voltage source as shown in Figure 1. These connections provide a direct way to manipulate the electrode potential *i.e.* the electrons' electrochemical potential within the bulk of the electrode material.[3, 4] The external connections and the working electrode (M) are physically distinct phases, which can be viewed as a statistical mechanical bath and system, respectively. In this perspective, constant electrode potential experiments correspond to controlling the electron reservoir/bath electrochemical potential, $\tilde{\mu}_e^{bath}$, and the system potential, $\tilde{\mu}_e^M$, responds to this change. At thermodynamic equilibrium, the electrochemical potentials of the connections and the working electrode are equal and electrochemical balance $\tilde{\mu}_e^{bath} = \tilde{\mu}_e^M$ is satisfied.[3, 5] The electrochemical potential of electrons in phase i can be written as

$$\tilde{\mu}_e^i = \mu_e^{0,i} - \phi^i \quad (1)$$

where $\mu_e^{0,i}$ is an intrinsic material property and ϕ^i is the inner potential *i.e.* electrostatic potential of phase i . Given that $\mu_e^{0,i}$ is constant for a given phase and material, the applied electrode potential on either *bath* or M is determined by the inner potential of a given phase.[5] Finally, we note that the electrochemical potential of electrons is directly proportional to the Fermi level of a given phase as $\tilde{\mu}_e = E_f$.

To mimic electrochemical experiments with atomistic simulations, several different schemes for controlling the applied potential have been put forth. Current methods to simulate the applied electrode potential can be roughly divided into three categories: electronic structure methods within the grand-canonical ensemble density functional theory (GCE-DFT)[6,

Figure 1: Depiction of a two-electrode cell with the relevant electrochemical potentials and the system explicitly treated in (GCE-)DFT simulations.

7], classical force field methods,[8] and finite-field approaches which can be used with both DFT and classical potentials.[9–12] GCE-DFT simulation typically treat a single electrode and work on the absolute electrode potential scale to fix $\tilde{\mu}_e$. Importantly, the grand canonical free energy as well as other (thermodynamic) expectation values from a GCE-DFT calculation are formally exact and unique to a given external (electrode) potential with an explicit dependence on $\tilde{\mu}_e$. [13–15]. As discussed in detail in Section 2.1, $\tilde{\mu}_e$ is directly related to the electrode work function or Fermi level[3] readily available from any periodic DFT implementation. Given this generality and ability work with just a single electrode at the DFT level, the GCE-DFT framework has been widely adopted for modelling electrochemical thermodynamics[14, 16–30] and kinetics[2, 26, 29, 31–33] at fixed electrode potentials.

Classical force field and finite field methods adopt a different approach to constant potential simulations.[8, 11, 34–39] These methods describe the applied electrode potential in terms of the inner potential (ϕ) difference between two electrodes[8–12, 34–39], and do not need any electronic structure information. This attractive feature, however, comes with a cost as two electrode interfaces need to be simulated to build an electrode potential difference in the cell and keep the simulation cell neutral. As one is typically interested in the properties of just a single electrode, *i.e.* the working electrode, the second electrode acts as a passive counter electrode. While the treatment of a passive electrode is justifiable for low-cost analytic force field potentials, this argument does not hold with electronic structure methods or even machine learning potentials as their computational cost is two or three orders-of-magnitude larger than that of analytic classical potentials.[40] Therefore, future studies of

electrochemical interfaces with machine learning potentials need new approaches enabling constant potential calculations of single electrodes without electronic structure information

Both GCE-DFT and classical force field methods have thus far overlooked the question of which electrochemical potential, $\tilde{\mu}_e^{bath}$ or $\tilde{\mu}_e^M$, is the relevant quantity to fix in GCE-DFT simulations. While this has not been considered in the context of computational electrochemistry, the recent work by Islas-Vargas *et al.*[41] addressed this in detail for semiconductors and emphasized that the relevant thermodynamically independent parameter in GCE-DFT is the bath chemical potential ($\tilde{\mu}_e^{bath}$) and not that of the system ($\tilde{\mu}_e^M$). As we will shown in this work, this distinction is crucial for GCE-DFT methods as the system’s Fermi level (E_f^{DFT}) obtained from electronic DFT calculations is not necessarily the correct independent thermodynamic variable in GCE-DFT if $\tilde{\mu}_e^M = E_f^{DFT} \neq \tilde{\mu}_e^{bath}$. This inequality has already been demonstrated for semiconductor electrodes[41] where it results from neglecting the metallic connections in the simulation cell. So far all GCE-DFT implementations of metallic and semiconductor electrodes have explicitly fixed $\tilde{\mu}_M$ or E_f^{DFT} , which are not generally equal to the experimentally modulated $\tilde{\mu}_e^{bath}$. In other words, constant Fermi level simulations reflect fixing the electrochemical potential of the *simulation cell*, not that of the connections and electrode bulk controlled experimentally. While the distinction between $\tilde{\mu}_e^{bath}$ and $\tilde{\mu}_M = E_f^{DFT}$ might appear insignificant, we will show that these electrochemical potentials are indeed different when simulating other systems than metallic electrodes and strongly adsorbed species (inner-sphere reactions) considered thus far. In particular, it will be demonstrated that $\tilde{\mu}_e^M = \tilde{\mu}_e^{bath} = E_f^{DFT}$ only for metallic electrodes and inner-sphere reactions whereas $\tilde{\mu}_e^M = E_f^{DFT} \neq \tilde{\mu}_e^{bath}$ for several relevant electrochemical systems such as semiconductor electrodes, biased two-electrode cells, or outer-sphere redox couples interacting weakly with the electrode. The observations made in this work show the limitations of current constant Fermi level methods and call for more general GCE-DFT methods where $\tilde{\mu}_e^{bath}$ rather than E_f^{DFT} is explicitly controlled.

To achieve this, we introduce a new constant inner potential (CIP) DFT method, and demonstrate its performance as a general and theoretically rigorous approach to constant potential *ab initio* simulations. Importantly, CIP simulations directly control $\tilde{\mu}_e^{bath}$, which enables GCE-DFT simulations even for systems where the constant Fermi level methods

do not reflect the experimentally applied potential. The CIP expands the scope GCE-DFT simulations to semiconductor electrodes, outer-sphere reactions and a biased two-electrode cells. By theoretical arguments and diverse examples, we show that CIP emerges as a universal approach for simulating a wide variety of electrochemical systems from metallic to semiconductor electrodes and from inner-sphere to outer-sphere reactions under constant electrode potential or bias within GCE-DFT.

2 Results

2.1 The inner potential as the basic variable in GCE-DFT

We start by introducing the theoretical concepts behind using the electrode inner potential as the basic variable to control the applied potential in GCE-DFT simulations. The GCE-DFT methods developed thus far have controlled E_f^{DFT} to account for the electrode potential on the single electrode scale.[3, 42] This is not, however, the only possibility for GCE-DFT calculations as at least four different single potential definitions are possible depending on the chosen reference for the potential.[3] The most general definition of a single electrode potential is

$$U^M(abs) = \Delta_S^M \phi - \mu_e^{0,M} + K \quad (2)$$

where $\mu_e^{0,M}$ is an intrinsic materials property and independent of the electrode potential. $\Delta_S^M \phi = \phi^M - \phi^S$ is the difference of inner potentials *i.e.* electrostatic potential differences between the bulk of electrode (M) and solution (S) as shown in Figure 2 while K is a constant depending on the chosen scale. The reference for K used in all previous GCE-DFT approaches[42] is the electrostatic potential in the vacuum in which case $U_{vac}^M(abs) = -\tilde{\mu}_e^M = -E_f^{DFT}$. [3, 43] The CIP method developed herein uses a different reference scale where $K = \mu_e^{0,M}$, which allows controlling $\Delta_S^M \phi$ directly without introducing the Fermi level explicitly.

While the $K = \mu_e^{0,M}$ scale is not experimentally viable, we show that this scale is natural for DFT simulations and leads to CIP-DFT. In experiments and under thermodynamic equilibrium, it is guaranteed that the system and bath electrochemical potentials are equal

($\tilde{\mu}_e^M = \tilde{\mu}_e^{bath}$) because both the connections and the working electrode are explicitly present (see Figure 1). As $\mu_e^{0,i}$ is an intrinsic property of phase i , the electrochemical potential of electrons is experimentally controlled by modulating the inner potential within the bulk phases of M or $bath$. [3, 5] Crucially, changes in the bath inner potential, $\Delta\phi^{bath}$, uniquely define the response of the system inner potential $\Delta\phi^M$ under equilibrium conditions because both are innate bulk properties. [44] This highlights that the applied electrode potential directly modifies ϕ^M .

These arguments hold for both metallic and semiconducting (SC) electrodes [3, 5, 44] but in semiconductors the finite number of charge carriers and their spatial concentrations need to be accounted for. [45, 46] The semiconductor electrode potential is still controlled by the bulk of the electrode through metallic connections but the Fermi level has a more complicated expression due to the limited number of charge carriers: [45, 46] $E_f^{SC} = -V_H - \chi - V_{sc} - \zeta$ which depends on the electrostatic potential drop within the semiconductor (V_{sc}) and the Helmholtz layer (V_H), conduction band position through the electron affinity χ , and the amount of doping ζ in the bulk phase. E_f^{SC} can be converted to an experimental scale through Eq. (2). In addition to the dependency on doping and the need for describing potential drops both within the electrode and at the interface, the DFT simulations of semiconductor electrodes are further complicated by the varying conventions of defining the E_f^{DFT} and the use of finite-size slab models. For instance, some codes use the valence band as E_f^{DFT} whereas others place it in the band gap. Simulations with slab models omit the metallic connections, the treatment of (charged) bulk defects as well as their effect on the Fermi level for the sake of computational efficiency. Such discrepancies between the experimentally used semiconductor electrodes and their computational models combined with complex definition of semiconductor electrode potentials have led some authors to consider that the semiconductor electrode potential cannot be continuously altered [47] in GCE-DFT simulations due to the presence of the band gap.

The electrode potential discontinuities are, however, a computational artefact related to the use of E_f^{DFT} and the confusion between system and bath electrochemical potentials in GCE-DFT calculations. [41] Instead of working with E_f^{DFT} , a more robust description of semiconductor electrode potentials without discontinuities in GCE-DFT calculations can be

Figure 2: Illustration of the CIP. The inner potential within in the electrode (ϕ^M) can be controlled and fixed to a specified value. The solution inner potential ϕ^S is always fixed at zero.

obtained using the semiconductor inner potential. The applied electrode potential can then be written in terms of the local electrostatic potentials and material-dependent constants.[5, 45, 46] Hence, the applied semiconductor electrode potential (ΔU) is directly proportional to the bulk electrostatic potentials *i.e.* inner potentials at different charge states[45, 46, 48]

$$\Delta U = -\Delta E_f^{SC} = \Delta \phi^{bulk} \quad (3)$$

Therefore, the applied potential of a semiconductor electrode can be controlled through the bulk electrostatic potential in accordance with Eq. (2) in complete analogy with the metallic electrodes.

The above discussion highlights the central role of the electrode inner potential in modelling the applied electrode potential in electrochemical systems. This is also supported by the general theory of single electrode potential in Eq. (2). Furthermore, the inner potential is a local quantity which allows controlling the electrode potential between bulk phases (either solid, liquid, or gas) as shown by the various examples in Sections 2.2-2.6 below. The use of $\Delta_S^M \phi$ therefore ensures that the experimentally applied potential *i.e.* $\tilde{\mu}_e^{bath}$ is directly mimicked, quantities inherent to the used DFT simulation cell ($\tilde{\mu}_e^M = E_f^{DFT}$) are avoided.[41]

To control the electrode inner potential in GCE-DFT simulations, we introduce the constant inner potential (CIP) GCE-DFT calculations illustrated in Figure 2. The CIP method has been implemented in the GPAW[49, 50] code by modifying the solvent jellium model (SJM).[26] The original SJM model controls E_f^{DFT} and CIP-DFT extends SJM to fix the

inner potential ϕ^M against the solution inner potential ϕ^S . By using Dirichlet boundary, the solution inner potential is fixed to zero ($\phi^S = 0$). As displayed in Figure 2, controlling ϕ^M while keeping ϕ^S fixed results in a well-defined electrode potential and constant reference point. In principle and practice, there is no need to introduce the E_f^{DFT} to define the absolute potential as the inner potential uniquely defines the electrode potential and ϕ^M can be converted to an experimental scale. A more detailed description of the CIP-DFT method is available in the Supporting Information. In the following sections we demonstrate the performance of CIP-DFT for simulating a wide variety of electrochemical systems ranging from inner-sphere reactions on metallic electrodes to outer-sphere reactions, semiconductor electrodes, and the creation of a biased two-electrode setup. Furthermore, we show that the method can be combined with both explicit and implicit solvent models.

2.2 Inner-sphere interactions

The CIP approach is first applied to study the pristine and oxygen-covered Au(111) surface at different potentials and surfaces charges. This presents an electrochemical system of a metal electrode interacting strongly with an adsorbate and is an example of an inner-sphere interaction. Figure 3 displays the electrostatic potentials and Fermi levels for bare and oxygen-covered gold surfaces at different surface charges/electrode potentials. Comparison of the Fermi level and gold’s inner potential differences shows that the same surface charge density leads to the same electrode potential difference from both methods. The density of state (DOS) analysis displayed in Figure 3c shows that the DOS at and close to the Fermi level is dominated by gold atoms indicating that changes in the Fermi level modify the electrochemical potential of electrons primarily within the electrode as expected.

In addition, we see that in the presence of oxygen, the Fermi level has contributions from gold-oxygen interaction and that it might not be uniquely determined by the electrode bulk. However, the electrostatic potentials in Figure 3 show that the inner potential maxima and the Fermi level coincide perfectly for both the pristine and adsorbate-covered Au surfaces. This indicates that the standard chemical potential ($\mu_e^{0,Au}$) and the inner potential (ϕ^{Au}) are determined by the gold electrode bulk. Therefore, the electron’s electrochemical potential ($\tilde{\mu}_e^{Au} = \mu_e^{0,Au} - \phi^{Au}$) and the Fermi level of the system are determined by the Au bulk. Hence,

Figure 3: a) xy-averaged electrostatic potentials and Fermi levels for the pure (b) and oxygen covered (c) Au(111) surfaces at three different surface charges, the orange curve corresponds to the potential of zero charge (PZC) simulation while the green (black) curves have surface charges $\sigma = 0.05e$ ($-0.05e$). The grey region depicts the area in which the electrode inner potential is computed. The insets show the electrostatic potentials within the electrode and Fermi level. c) The DOS plot for the $\sigma=0.05e$ with the red dashed line indicating the Fermi level

in this case, the system and bath electrochemical potentials coincide, and Fermi level and CIP approaches are equally suitable for GCE-DFT simulations.

2.3 CIP molecular dynamics

As a second example we demonstrate the simulation of an explicitly solvated Au(111) interface presented in 4 using both constant inner potential (CIP-DFT) and constant charge (canonical DFT) molecular dynamics (MD). In general, the results in Figure 5 demonstrate that the CIP-DFT-MD calculations can readily be performed to study the dynamics of ex-

Figure 4: The setup used for the molecular dynamics simulations of the Au(111)-water interface.

Figure 5: a) Fermi level and inner potential fluctuations as a function of the simulation time for solvated Au(111) surface at a surface charge of $-0.2e/88\text{\AA}^2$. Both values are referenced against respect quantities of the 500th frame. b) CIP-DFT molecular dynamics for the solvated the Au(111) surface. The inner potential is fixed to -14.0 eV with ± 0.1 eV fluctuations corresponding to $+0.6$ vs. Au(111) the PZC.

plicitly solvated electrochemical interfaces and that even moderately large systems can be simulated to address the dynamic interfacial properties under constant (inner) potential conditions. By comparing the number of MD steps in constant potential and constant charge simulations against wall-time, the constant potential simulation was observed to be $\sim 20\text{-}25\%$ more time consuming but not prohibitively expensive as sometimes assumed.[51]

Figure 5a shows the Fermi level and inner potential variations in fixed charge calculations for the solvated Au(111) interface as a function of time and demonstrates that they are practically indistinguishable. This indicates that the Fermi level of a solvated Au(111) is almost fully determined by the electrode and the Fermi level resides on the electrode even when small hybridization between the surface and water takes place. In practice both the Fermi level and inner potential approaches are equally suitable for describing the Fermi level in this case. While this is an expected observation, it differs from the recent results in Ref. [52] where the Fermi level and $\Delta_S^M \phi$ surprisingly exhibit different fluctuations in fixed charge calculations. As discussed in detail in the Supplementary Information and throughout the manuscript, E_f and $\Delta_S^M \phi$ should yield the same (thermodynamic) expectation values, fluctuations, and electrode potentials for systems where the Fermi level is dominated by a metallic electrode.

While the same thermodynamic expectation values are obtainable from either grand canonical (constant potential) or the canonical (constant charge) simulations, the variations and fluctuations in (thermodynamic) variables are not the same in different ensembles.[53] From a fundamental point of view, variations and fluctuations around equilibrium values are central properties in statistical thermodynamics needed to ensure thermodynamic consistency. For DFT studies this means that GCE-DFT simulations are needed for a fully consistent treatment of the electrochemical interfaces. More practical motivation for the use of GCE-DFT-MD to simulate electrochemical reactions include *e.g.* the importance of thermal fluctuations on adsorption energies[54] and fluctuations in diabatic energy gaps determining the reaction rate in Marcus-like (proton coupled) electron transfer theories.[32, 55] Figure 5b demonstrates that the CIP-DFT calculations for the explicitly solvated interface at constant electrode potential exhibits substantial charge fluctuations which play an important role in computing *e.g.*, electrochemical reaction barriers and prefactors within

2.4 Outer-sphere reactions

Thus far, all GCE-DFT studies in electrochemistry have focused on inner-sphere reactions while the important class of outer-sphere reactions has not been addressed and they remain only partially understood.[57] It is typically assumed that outer-sphere couples do not strongly interact or hydridize with the electrode so that the total system can be considered as a weakly interacting combination of the electrode and solvent-phase subsystems. Here, we consider a classical outer-sphere redox couple $\text{Ru}[\text{NH}_3]_6^{3+}$ on a Au(111) surface as depicted in Figure 6. As the electrode and redox couple belong to different phases, it should be possible to control their properties separately and to modulate the electrode potential independent of the solution phase as demonstrated in Figure 6. As long as the electrode Fermi level is above the $\text{Ru}[\text{NH}_3]_6^{3+}$ reduction potential (≤ -4.6 V), the Fermi level from a DFT calculation (E_f^{DFT}) should mainly be defined by the electrode. However, when the Fermi level is below the reduction potential, E_f^{DFT} would nominally reside on the solution phase redox couple; in this potential range E_f^{DFT} does not "belong" to the electrode alone and cannot be controlled independently from the solution phase.

Figure 6: Electrochemical potentials for the Au(111) electrode and the $\text{Ru}[\text{NH}_3]_6^{3+/2+}$ redox couple on the absolute electrode potential scale[3]. At -4.44 V, the Fermi level of the simulation cell is determined by the electrode whereas at the Au(111) PZC at -4.96 V the Fermi-level is defined by the $\text{Ru}[\text{NH}_3]_6^{3+/2+}$ couple.

In order to understand the Fermi level and inner potential variations in self-consistent

DFT simulations for outer-sphere reactions, the total charge in the simulation cell was varied in a broad range corresponding to the potential range of ± 1.0 V around the reduction potential of $\text{Ru}[\text{NH}_3]_6^{3+}$. Note that $\text{Ru}[\text{NH}_3]_6^{3+}$ charge is always +3 independent of E_f^{DFT} because constrained DFT was used for controlling the charge state (see Section 4). The molecular orbitals in Figures 7a-d show that the redox couple and the electrode are strongly hybridized, and cannot be separated into two subsystems in self-consistent GCE-DFT simulations. This is also visible in the DOS provided in Figure 7e which shows that the electronic states around the Fermi level contain a significant contributions from $\text{Ru}[\text{NH}_3]_6^{3+}$ despite the use of constrained DFT to obtain the correct +3 charge on the redox couple. The electronic states residing on the redox couple are present at all energies around -0.2 eV in the DOS plot for almost all charge states. Only when the simulation cell carries a significant negative charge is the Fermi level (line "-3.58" in Figure 7) determined exclusively by the electrode.

Figure 7: Ru[NH₃]₆³⁺ on the Au(111) surface. a)–d) (HOMO-1) – (HOMO+2) orbitals when $E_f = -4.46$ eV. e) Projected DOS and zoom of the DOS around the Fermi level. f) Electrostatic potentials (solid lines), inner potentials (dashed line) and Fermi levels (dash-dotted lines) at different surface charges and¹⁴ corresponding absolute potentials.

The substantial contribution of $\text{Ru}[\text{NH}_3]_6^{3+}$ to the DOS around the Fermi level suggest that E_f^{DFT} cannot be controlled independent of the solution phase. The variations in E_f^{DFT} and the gold inner potential (ϕ^{Au}) as a function of the charge given in Table 1 show that this is indeed the case; the electrode potential variations inferred from ϕ^M and E_f^{DFT} are rather small but systematically different. The charge state changes have a consistently larger impact on E_f^{DFT} than ϕ^{Au} . This observation is attributed to the large number of electronic states residing on the redox couple at the Fermi level and means that a certain charge in the simulation cell does not exclusively localize on the electrode but also on the solvent phase species. For the $\text{Ru}[\text{NH}_3]_6^{3+}$ -Au system the electrode potential differences between the two approaches are within 0.1 V and correspond to $\sim 5\%$ differences in the applied electrode potential. For quantitatively accurate calculations this is already a notable difference and the 5% error in the over-potential η leads to a factor of 7 or 3 error in the computed reaction thermodynamics and rates (from $\exp(-\Delta G/k_B T) = \exp(-\Delta \eta/k_B T)$ and Butler-Volmer equation with symmetry factor 0.5). We expect that even larger differences will occur for electrodes such as graphene with a low DOS around the redox potential, densely charged anionic outer-sphere species such as O_2^- , or when a very limited number of atoms is to present the electrode. The differences between Fermi level and inner potential control are also expected become more pronounced when the surface PZC and the redox potential of the outer-sphere couple differ significantly as results in Table 1 indicate that the differences between Fermi level and inner potential potential methods increase as the system is more charged.

The reasons for the electrode potential differences obtained from ϕ^{Au} and E_f^{DFT} can be understood from the results in Figure 7. This Figure shows that the electrostatic potential maxima within Au and the Fermi level do not coincide for the $\text{Ru}[\text{NH}_3]_6^{3+}$ interacting with Au(111). Instead, there is a non-constant difference between the inner potential maxima and E_f^{DFT} at the same charge state, which leads to different electrode potential changes inferred from the two methods. This further emphasizes the fact that E_f^{DFT} is not uniquely determined by μ_{Au}^0 and ϕ^{Au} but has sizable contributions from $\text{Ru}[\text{NH}_3]_6^{3+}$. Instead, ϕ^{Au} is by definition uniquely determined by the bulk of the electrode at all charge states because the electrostatic effects between $\text{Ru}[\text{NH}_3]_6^{3+}$ and Au(111) are efficiently screened within the

gold electrode even when hybridization takes place.

Overall, our results demonstrate that in outer-sphere interactions, the system and bath electrochemical potentials are no longer equal because $\tilde{\mu}_e^M = E_f^{DFT}$ has contributions from the redox couple. As an outer-sphere redox couple is not directly coupled to the electron bath *via* external connections, such species should not contribute to the electrode potential according to Eq. (2) and electrode potential variations should only result from inner potential differences, $\Delta\phi^M$. Therefore, the inner potential control and the CIP approach are consistent with the general electrode potential definition whereas electrode potentials inferred from E_f^{DFT} do not reflect the state of the electrode *alone* but the entire simulation system. As ϕ^M is not affected by the solution phase redox species and because $\Delta\phi^M = \Delta\phi^{bath}$ holds under equilibrium,[44], CIP can correctly mimic the bath's electrochemical potential ($\tilde{\mu}_e^{bath}$) controlled experimentally. Therefore, the CIP approach provides a more general and theoretically robust way to simulate electrochemical outer-sphere reactions.

ΔE_f^{DFT}	$\Delta\phi^{Au}$	$\Delta E_f^{DFT} - \Delta\phi^{Au}$
0.88	0.82	0.06
0.45	0.43	0.02
0.00	0.00	0.00
-0.32	-0.31	-0.01
-0.70	-0.68	-0.02
-1.13	-1.09	-0.04
-1.52	-1.47	-0.05

Table 1: Comparison of the electrode potential differences for $\text{Ru}[\text{NH}_3]_6^{3+}$ on the Au(111) surface computed from Fermi levels (ΔE_f^{DFT}) and inner potentials ($\Delta\phi^{Au}$) compared with the $E_f = -4.44\text{eV}$ and the corresponding ϕ^{Au} . All values are in eV.

2.5 Semiconductor electrodes: TiO_2

Simulations of the semiconductor electrode potential are expected to exhibit large differences between the Fermi level ($\tilde{\mu}_e^M = E_f^{DFT}$) or the bath electrochemical potentials ($\tilde{\mu}_e^{bath}$) as these quantities are not generally equal.[41] As discussed in detail in the supplementary Section

S5, E_f^{DFT} is not continuous in the semiconductor band gap whereas experimentally applied electrode potential is continuous because one controls the bath electrochemical potential $\tilde{\mu}_e^{bath}$. Neglecting the differences between these two electrochemical potentials has led to a misconception seems the electrode potential and charge state cannot be changed continuously in GCE-DFT simulations of semiconductors.[47] This is true, however, only for $\tilde{\mu}_e^M = E_f^{DFT}$ based GCE-DFT whereas constant inner potential control calculations enable varying the applied potential continuously.

This is demonstrated for the pristine anatase-structured $\text{TiO}_2(101)$. The DOS plots in Figure 8a show that TiO_2 has a sizeable band gap at the DFT+U level of theory and the band edges are not determined by the surface atoms. Introducing only ± 0.05 electrons in the system changes E_f^{DFT} by $\sim \mp 1.0$ eV with respect to the neutral reference system whereas the inner potential changes are much smaller ($\sim \mp 0.3$ eV) and of similar magnitude as the changes observed for the metallic electrodes above. This example highlights that electrode potential in GCE-DFT methods controlling E_f^{DFT} is very sensitive to the number of electrons, which greatly hampers convergence to the desired electrode potential. On the hand, the inner potential response to the charge is continuous, which facilitates the convergence of CIP-DFT to the chosen electrode potential.

Figure 8: a) $\text{TiO}_2(101)$ DOS at different charge states of 0.00 ($E_f = -5.34$) and ± 0.05 e. The filled plots show the PDOS on the surface atoms. b) Electrostatic potentials and Fermi levels at the same charge states.

Besides facilitating GCE-DFT convergence, the semiconductor inner potential and con-

sequently the CIP method are directly proportional to the applied electrode potential shown in Eq. (3) and discussed in Section 2.1. As the experimentally applied potential is uniquely defined by $\tilde{\mu}_e^{bath}$ [41], the applied potential can corresponds to changes in the inner potential ϕ^M ($\Delta\tilde{\mu}_e^{bath} = -\Delta\phi^M$) Therefore, the CIP approach offers control over the applied electrode potentials also in semiconductor electrodes whereas the constant E_f^{DFT} GCE-DFT suffers from the discontinuities in the electrode potential and numerical difficulties as discussed above.

2.6 Biased two-electrode setups within DFT

Our final examples demonstrates the construction of a biased two-electrode electrochemical cell and a molecular junction. Such configurations are common in electrochemical experiments, in classical force field simulations of electrochemical interfaces, and quantum transport studies of molecular junctions. However, modelling the bias in such configurations with DFT-based electronic structure is difficult as E_f^{DFT} does not reflect the potential of a single electrode but that of the entire simulation cell. In fact, ground state DFT is formally an equilibrium theory which does not permit two different Fermi levels in the same simulation cell[58] and doing so would formally require utilizing more advanced techniques such as non-equilibrium Green’s function methods.[59, 60]. Recent studies have, however, shown that a Fermi level difference between two electrodes can be induced using localized molecular orbitals either within the tight-binding DFT approximation[61] or using the novel multi-space DFT[62–64] (MS-DFT) approach (see Supporting information S4 for more discussion on MS-DFT). Both of these methods require the use of localized orbitals limiting their applicability in solid-state DFT codes typically employing either a plane-wave or a real-space grid basis.

We use CIP and constrained DFT (cDFT) to overcome these restrictions and model biased interfaces with real-space methods without localized basis functions or Wannier-localized orbitals using the methods detailed in Section 4 and Supporting information Section S4. In the first example, a two-electrode cell consisting of two separated Au(111) electrodes are modelled using the configuration in Figure 9a. The electrode potential difference or bias between the gold surfaces was achieved by using cDFT to induce a localized external 1eV potential within the ”right” electrode. As demonstrated by Figure 9a, the cell E_f^{DFT} is set

by the left electrode and is constant in the unit cell. In particular, Figure 9a shows that the local external potential induces a $\Delta\phi = -(\phi_{right} - \phi_{left}) = 1.03V$ bias between the two electrodes demonstrating that electrode potential difference in a two-electrode cell can be realized with CIP-cDFT. Furthermore, through the use of Dirichlet boundary conditions on the right cell boundary, the electrode potential of both electrodes can be expressed on the absolute electrode potential scale and converted to experimental scales (see Supporting information Section S2).

Figure 9: a) Inner potentials (dashed) for the two gold electrodes. b) An 1,4-dithiol-phenylene molecular junction under constant bias.

Figure 9b gives another example of using CIP-cDFT method for a biased two-electrode cell of a 1,4-dithiol-phenylene molecule sandwiched between two gold electrodes. cDFT was employed to localize a $+0.5$ eV (-0.5 eV) external potential on the left (right) electrode, which creates a non-equilibrium electron density distribution between the two electrodes and a bias across the molecular junction. By comparing the equilibrium and non-equilibrium electrostatic potentials from DFT and cDFT, respectively, we observe that the application of cDFT results in a 1 V bias ($\Delta\phi_{DFT-cDFT} = 1$) across the 1,4-dithiol-phenylene junction. This finding is in very good agreement with the more elaborate MS-DFT method (see Figure 2 of Ref. [62]). Supported by on the detailed analysis of CIP-DFT and MS-DFT in the Supporting information Section S4 we conclude the CIP-cDFT describes the *bias across an electrochemical cell* with similar accuracy to the more involved Green's function methods or MS-DFT. The CIP-cDFT approach therefore provides a solution to the long-standing

issue[60] of simulating a finite bias in two-electrode cell using DFT.

3 Discussion

The above examples illustrate the performance and generality of the CIP-DFT method developed herein. The broad applicability of the method stems from its foundation in the rigorous definition of (single) electrode potentials (see Eq. (2)). In CIP-DFT, the electrode inner potential, ϕ^M , is directly controlled which allows fixing the electron bath electrochemical potential ($\tilde{\mu}_e^{bath}$) because changes in ϕ^M are equal to changes in the bath electrochemical potential.[44] This also, shows that ϕ^M is the thermodynamically relevant independent parameter in GCE-DFT and the quantity defining the experimentally applied electrode potential. These features make the CIP-DFT method different from the usually applied GCE-DFT simulation methods, where the Fermi level (E_f^{DFT}) of the simulation cell is fixed. Through several examples we have shown that controlling ϕ^M rather than E_f^{DFT} makes CIP-DFT a widely applicable method to computationally study electrochemical systems at constant electrode potential even in situations where the constant E_f^{DFT} method does not accurately mimic the applied electrode potential.

For metallic electrodes and inner-sphere reactions on metal electrodes, the CIP approach gives equivalent results with the widely adopted constant Fermi level description. However, for outer-sphere reactions and semiconductor electrodes the, two approaches yield different electrode potentials. In outer-sphere reactions, E_f^{DFT} no longer "belongs" to the electrode alone and consequently the Fermi level is not uniquely determined by the electrode whereas ϕ^M on the contrary is locally defined within the electrode and the outer-sphere couple has no effect on it. Therefore, ϕ^M can be controlled independently from the solvent phase in line with experiments and the general definition of electrode potentials (Eq. (2)). E_f^{DFT} on the other hand depends on the presence of the redox couple and does not reflect experimental electrode potential control. For semiconductor electrodes, the advantages of using ϕ^M are different. Most importantly, ϕ^M can be controlled continuously and it is comparatively less sensitive to the number of electrons, whereas E_f^{DFT} varies discontinuously in the band gap region and exhibits large jumps when the number of electrons is changed. This difference

arises from the ability of CIP to control the electron bath electrochemical potential ($\tilde{\mu}_e^{bath}$) while the computed Fermi level is inherent to the simulation cell ($\tilde{\mu}_e^M$) and does not reflect the applied electrode potential in semiconductor materials. Consequently, we find the CIP-DFT method to be more suitable than E_f^{DFT} -based GCE-DFT for constant potential *ab initio* calculations for large classes of outer-sphere reactions and semiconductor electrodes

We have also shown that by combining CIP and constrained DFT, electrode potential difference or bias between two electrodes can be induced in a DFT simulation cell. This is simply not possible with E_f^{DFT} -based GCE-DFT approaches. Simulating the bias between two electrodes will open new possibilities in simulating the applied electrode potential in two-electrode electrochemical cells at the DFT level[60, 65] and non-equilibrium charge transfer through single-molecule junctions without Green’s function techniques (see Supplementary section S4)[62]. Other important uses of CIP-cDFT include *e.g.* hindering unphysical instantaneous electron transfer events [66] and modelling the explicit bias in STM simulations.[67] A particularly useful aspect of the CIP-cDFT is that the bias potential can be built without using local orbitals making the method compatible with plane-wave or real-space codes. The cDFT method is already available in several solid-state DFT codes making the CIP-cDFT widely applicable with minimal implementation work.

The utilization of inner potentials can also have other surprising advantages and bridge concepts utilized in DFT and classical force field -based simulations of electrochemical interfaces as discussed in Section 1. It was shown that only the electrode and solvent inner potentials are needed in both DFT and force field simulations making CIP a unified scheme for constant potential simulations. In particular, ϕ^M rigorously models the applied electrode potential and the CIP method does not in principle require any knowledge about the electronic structure; ϕ^M can be extracted from charge distributions obtained with either classical or a quantum mechanical simulations. This means that the CIP approach can faithfully describe the electrode potential even without electronic structure information and utilize a single-electrode description to achieve lower computational cost. We consider that this feature makes CIP a very promising method for describing the electrode potential without electrons using machine learning potentials, which account for long-range interactions and atomic charges.[68–72] Future work combining CIP and machine learning potential

may altogether avoid the description of electrons in electrocatalysis to utilize machine learning potentials for all regions and atoms beyond current QM/MM DFT/reactive force field methods[73]. We expect that the CIP method will find broad applicability in simulating the applied electrode potential in several challenging electrochemical systems ranging from inner-sphere to outer-sphere reactions, metallic to semiconducting (photo)electrodes, and to biased electrochemical cells.

4 Computational methods and models

All simulations were made using the GPAW software.[49, 50, 74]. The wave functions were presented on a real-space grid with 0.18 Å grid spacing. The PBE functional[75] was used in all simulations. The solvent was modelled using the SCMVD dielectric continuum model[76] with the van der Waals radius of 2.0 Å for gold to accurately reproduce the differential capacitance of gold.[14] Constant potential calculations, both in the standard Fermi level and the new constant inner potential modes, were carried out using a modified SJM implementation.[26] All models were periodic in the xy-directions and non-periodic in the z-direction. Dirichlet boundary conditions were utilized to achieve $\phi = 0$ at z-boundary at all charge states as detailed above (see Supplementary Information) – this uniquely defines a reference electrode within the simulation cell.[14]

As an inner sphere reaction, oxygen adsorption on a Au(111) hollow site was considered. The pure and oxygen-covered gold surfaces were modelled using a seven layer thick 1×1 surface cell. The k-points were sampled using a $10 \times 10 \times 1$ mesh.

The performance of CIP for constant potential calculations was demonstrated by a molecular dynamics simulations of an explicitly solvated Au(111) surface under both constant charge and constant inner potential conditions. This systems was presented with a $3 \times 4 \times 4$ Au(111) surface slab and 32 deuterated water starting from a pre-equilibrated structure from our previous work.[14] On top of the explicit water 8 Å of implicit water using the SCMVD model was included. Only the Γ -point is considered. The standard dzp-LCAO basis sets[77] were used for presenting the single-electron orbitals and density. The system was sampled by running canonical Langevin dynamics at 330K as implemented in ASE[74], and a 1fs

timestep and 5ps^{-1} friction coefficient were utilized. The electrode potential was referenced against the inner potential of the uncharged interface *i.e.* the potential of zero charge (PZC) through computing the inner potential within the two central layers of gold as show in Figure 4 (see also Supplementary Information). The system was kept neutral by placing an SJM counter charge in the implicit solvent part, see Figure 4.

A typical outer-sphere redox couple, $\text{Ru}[\text{NH}_3]_6^{3+}$, was considered in its oxidized +3 charge state. The simulated system is shown in Figure 6a and was modelled by placing $\text{Ru}[\text{NH}_3]_6^{3+}$ near a five-layer 5×5 Au(111) surface and using $2 \times 2 \times 1$ k-point mesh. The correct oxidized (3+) charge state on the redox couple at all fixed potentials was obtained by using the recent grand canonical ensemble constrained DFT (GCE-cDFT) method[32, 78]to constrain the +3 charge on $\text{Ru}[\text{NH}_3]_6^{3+}$. cDFT[79] applies a spatially localized external potential to obtain an *a priori* chosen distribution of charges in the simulation cell. The electrode potential was computed using the inner potential within the three inner gold layers. These potentials were converted to an experimental SHE scale using Au(111)’s PZC at 0.52 V vs. SHE using the as detailed in the Supplementary Information.

The semiconductor electrode was modelled as 4-8 layer anatase (101) TiO_2 surfaces Here the PBE+U functional with $U=4.5\text{eV}$ on the Ti d-orbitals was utilized. A $5 \times 5 \times 1$ k-point mesh was used. Here we show the results for a 4-layer model but the results for the 6 and 8-layer were quantitatively and qualitatively similar. Note, that this simple system is chosen to demonstrate the use of CIP for semiconductor electrodes and for more realistic calculations of semiconductor electrodes also defects, structural deformations etc. should be considered.

Construction biased two-electrode cells was illustrated for two gold slab separated by vacuum (Figure9a) or by a 1,4-dithiol-phenylene molecular junction (Figure9b). The configuration in Figure 9a consists of two $4 \times 4 \times 1$ gold slabs separated by $15 \text{ \AA}$ vacuum on both sides of the electrode. An electrode potential difference between the electrodes was induced with cDFT which introduces a localized external potential affecting only the "right electrode" in Figure 9. The molecular junction in Figure 9b was constructed from two $3 \times 3 \times 4$ Au(111) surfaces separated 1,4-dithiol-phenylene. On both sides of the Au slabs $8 \text{ \AA}$ of vacuum was added and only the Γ point was used. $+0.5 \text{ eV}$ (-0.5 eV) external cDFT potential was applied on the left (right) side to create a 1V electrode potential.

The dielectric solvent was not used in the two-electrode CIP-cDFT calculation due to extreme convergence problems caused by the finite-difference (FD) Poisson solver used in GPAW’s solvent and SJM models. The FD Poisson solver is known to be unstable for highly elongated cells such those as used for the two-electrode cell. Instead, the newly implemented FastPoissonSolver, which is the new default Poisson solver in GPAW, was observed to be stable and to provide converged results. However, FastPoissonSolver is not yet compatible with GPAW’s dielectric solvent models or the counter charges used in SJM. For this reason, the simulation cell was kept charge neutral and placed in vacuum and omitting the implicit solvent does not significantly alter the bias across the simulation cell.

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