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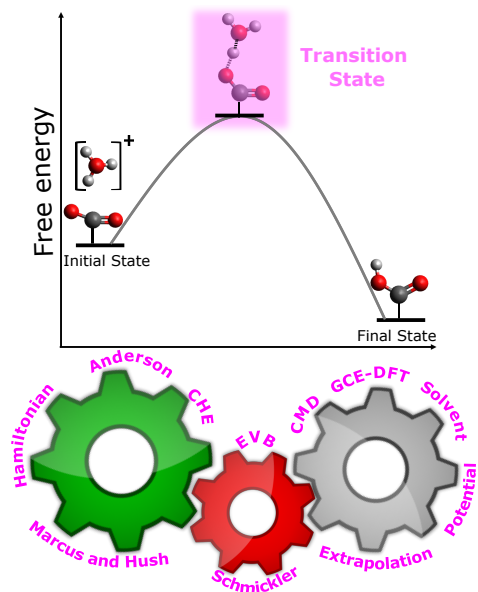


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Graphical Abstract

How are Transition States Modelled in Heterogeneous Electrocatalysis?

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Highlights

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- A consistent treatment of the adsorbate/surface, adsorbate/solvent and surface/solvent interactions is necessary for accurate activation energies
- Locating transition states for electrocatalytic reactions is now possible via model Hamiltonians, grand-canonical DFT, constrained molecular dynamics and combinations thereof

How are Transition States Modelled in Heterogeneous Electrocatalysis?

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Abstract

Electrocatalysis is a promising technology for clean energy conversion. The prediction of activation energies is essential for reliably modeling electrocatalytic processes. Currently a compromise is necessary between model complexity (electrochemical potential, electrode/electrolyte interface) and the accuracy of the resulting activation energies. We provide an overview on the approaches and recent advances in methods and models to identify transition states and thus activation energies in heterogeneous electrocatalysis, covering a large range of methods from model Hamiltonians to fully atomistic descriptions. We also discuss specific examples and highlight the strengths and weaknesses of each approach.

Keywords: Electrocatalysis, activation energies, transition states

1. Introduction

Converting electrical energy produced with low carbon emissions (e.g., wind and solar power), into chemicals such as hydrogen [1], ammonia [2] and CO₂ reduction products [3] seems very attractive to reduce the carbon footprint of the chemical industry. Therefore, the last two decades have seen a surge of interest in improving electrocatalysts. Concomitantly, computational chemistry has matured enough to accelerate the design of novel heterogeneous catalysts [4], especially when combined with experiments [5]. However, determining transition states for heterogeneous electrocatalysis is not straightforward and has remained a niche. The absence of reliable activation energies ultimately hampers the *in silico* design of electrocatalysts.

The thermodynamics of electrocatalytic reactions is well described via the Nernst equation: the electrochemical potential allows to drive reactions that

are endothermic under standard conditions. A first step towards the understanding of the kinetics of electrochemical reactions is provided by Marcus's theory:[6] For "outer sphere" electron transfer (i.e., no direct interaction between the reactant and the electrode, see Figure 1) the kinetics of the reaction is determined by the reaction free energy (ΔG) and the reorganization energy (λ). λ measures the energy required to adopt the product-like arrangement of the reactant and the surrounding solvent before the electron transfer. In heterogeneous electrocatalysis, the reaction is occurring at the interface between the solid electrocatalyst and the liquid electrolyte. Hence, the fundamental reaction step is an "inner sphere" electron transfer with a direct interaction between the reactant and the electrode (see Figure 1).[7] Due to the complexity and system specificity of the interface and the interaction of the reactant with the catalyst, the solvent and the electrolyte, the equivalent to the "universal" Marcus theory is absent for these inner-sphere processes.

Phenomenological rate equations have been developed to model the kinetics for inner sphere processes, with the Butler-Volmer equation being the most famous one. The reader interested in rate equations for electrocatalysis is referred to the thorough review in ref [8]. According to these equations, the reorganization energy is an important factor for the kinetics of inner sphere processes, but the coupling of the energy levels of the adsorbate and the electrode has to be considered as well. For example, the density of state around the Fermi level directly impacts the electron transfer, which means that the band-gap of semi-conductors is problematic in electrocatalysis [9]. Furthermore, the reactant competes with the solvent/electrolyte for the adsorption sites on the catalyst. Hence, the activation energy required for adsorption can be critical for the overall reaction kinetics.[10]

Even though the atomistic modelling of electrocatalysis has a long history, [11] it is only since the introduction of the computational hydrogen electrode (CHE)[12] by Norskov and co-workers that such studies are performed on a routine basis. The success of CHE is mainly due to its computational ease, which itself is derived from the assumption that only the thermodynamics of the reaction intermediates need to be considered, i.e., that identifying transition states is not necessary. The validity of this hypothesis has recently been revealed to be highly system-specific.[13] Given the excellent ratio of insight gained to computational expense of CHE, the modelling of transition states has been somewhat neglected by the community [5]. Nevertheless, quantitative experimental data on the relative stability of intermediates is

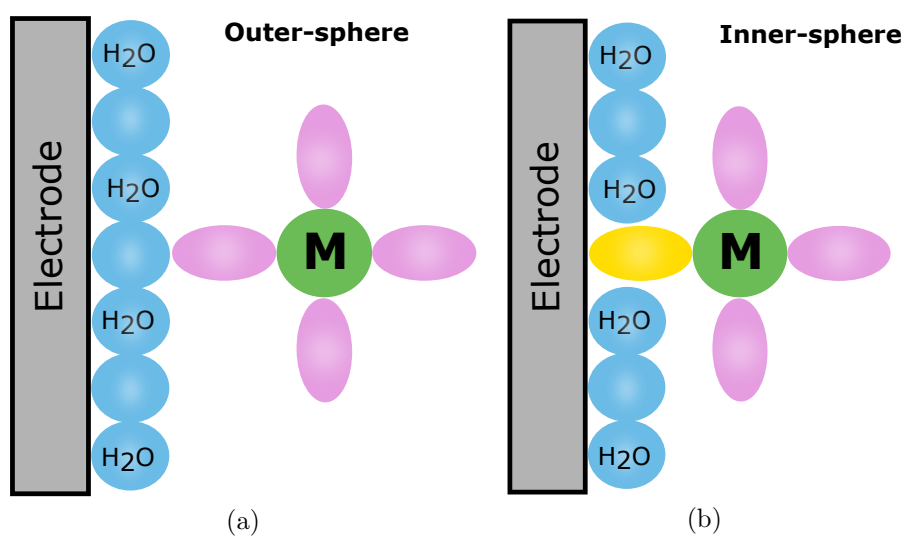


Figure 1: Schematic illustration of the mechanism of electrode reactions: (a) In an outer-sphere redox process, the reactant and product molecule (M) with its functional groups (pink) do not interact strongly with the electrode surface. (b) In an inner-sphere (catalytic) redox process, reactants, intermediates, and/or products interact strongly with the electrode surface (specific adsorption) and the electrode catalyzes the bond rearrangements for the functional group in contact with the catalyst (yellow).

unavailable, so that the quality of the approximations of the CHE cannot be precisely determined. In contrast, kinetic information (rates, Tafel slopes etc.) can be measured experimentally. Therefore, first-principles based kinetic simulations are required to validate theoretical models.[14, 15, 16] Thus, one has to determine (potential-dependent) activation energies and, therefore, identify transition states.[17] The potential-dependent activation energies are a first, necessary, step towards more approximate (linear-scaling-based) estimates that can then be used for catalyst screenings.[18, 19, 20] As discussed in the recent literature, [21, 13, 22] the success of the CHE-derived catalyst screenings without the consideration of potential-dependent surface states and activation barriers is at least partially a happy coincidence.

Electronic structure theory, such as density functional theory (DFT), is the tool of choice to determine activation energies from first principles. The electrode potential is equivalent to the workfunction, i.e., the energy to add/remove an electron to/from the system. For the popular CHE, DFT computations are performed at "constant charge", i.e., the number of electrons is fixed by the user and the workfunction is a result of the self-consistent field process. Alternatively (see section 3.3), in grand-canonical (GC) DFT the number of electrons is a variable that is adjusted to perform computations at "constant potential".[23, 24, 25] Thus, GC-DFT gives direct access to potential dependent activation energies. Note that only charge-neutral unit cells can be simulated by periodic DFT. Hence, in CHE the unit-cells are always neutral by construction and in GC-DFT a counter-charge (either uniform [26], based on the Poisson-Boltzmann equation or a combination thereof [27]) is included.

In combination with GC-DFT, modelling the solvent and electrolyte is necessary to achieve realistic capacities,[28, 29] the competitive adsorption between reactants and the solvent,[30] and electrolyte specific solvation environments. [31] Furthermore, the reorganization energy (λ), associated with a charge-transfer reaction, is one of the key components of the activation energy. Hence, solvation effects have to be carefully determined for activation energies in electrocatalysis. Unfortunately, however, accurately and efficiently treating solvation effects at solid/liquid interface remains an outstanding challenge.[32, 33, 34] Implicit solvation models are the most practical approaches, but have been found to significantly underestimate the solvation effects at metal/water interfaces.[35, 36, 37] This might be connected to the pronounced many-body effects of water molecules on noble metal surfaces,[38] which are inherently absent in implicit solvent models

that focus on electrostatic interactions.

In this review we outline the most relevant approaches to identify transition states and activation energies in heterogeneous electrocatalysis. We focus on the (physical or atomistic) model that describes the potential energy surface and only mention on passing the most important algorithms to actually identify the transition states. Furthermore, we do not reproduce any formulas, which can all be found in the original articles cited.

2. Potential Free Energy Surfaces from Model Hamiltonians

One possibility to understand the potential dependence of activation energies in electrocatalysis is to set up a "model Hamiltonian". This approach is perfectly illustrated by the work of Schmickler and co-workers.[39] Two ingredients are combined: (i) Marcus' theory for electron transfers that emphasizes the role of the reorganization energy λ . ii) The physical Anderson-Newns Hamiltonian for the interaction of adsorbates with the electrode.

In practice, a two or three dimensional potential energy is generated for electrocatalytic reaction, with the common choice of the dimensions being (i) the distance (z) of the center of mass of the molecule from the electrode, (ii) the bond distance (r), and (iii) the polarization state of the solvent (q), which corresponds to the total charge of the reactive complex. In Figure 2, the adsorbate is assumed to be in close (constant) contact with the electrode. The minimum at ($r = 0, q = 0$) corresponds to the physisorbed adsorbate (atomic orbital occupations ($\langle n \rangle$) of 2). When the two fragments are well separated ($r > 1.5$) a charge-transfer occurs ($q = 2$), leading to formally ionic adsorbates ($\langle n \rangle = 4$) on the surface.

Based on the PES, the minimum energy path (and thus the difference between the saddle point and the energy minimum, i.e., the activation energy) can then be identified by well established algorithms such as the nudged elastic band (NEB) or various string-based methods as is, for example, discussed in ref [40].

Just like in the theories of Marcus [41] and Levich-Dogonadze ([42]), it is the parametrization of the effective solvent coordinate q that represents the main challenge: $E(q)$ describes the energy change of the system as a function of the charge state of the system (before/after an electron transfer). The current approach consists of parameterizing the model Hamiltonian based on density functional theory (DFT) and molecular dynamics studies (MD). As mentioned in the introduction, determining accurate solvation effects at the

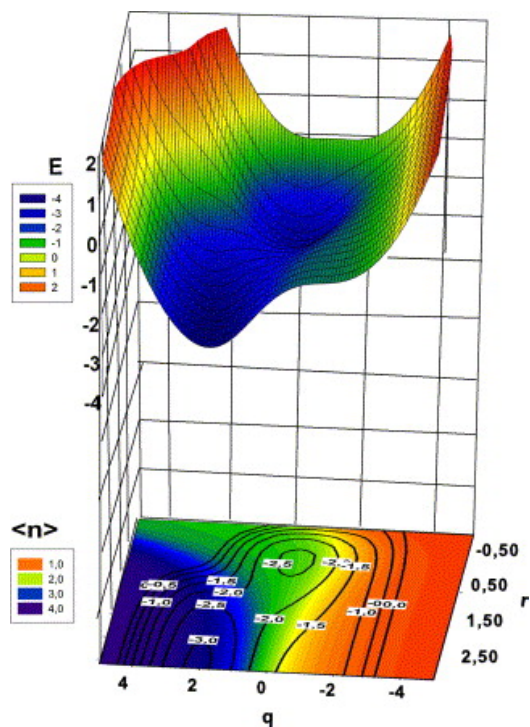


Figure 2: Schematic illustration of the mechanism of electrode reactions: Potential energy surface for a reaction of electron transfer and bond-breaking. The upper part shows the potential energy as a function of the solvent coordinate q and the deviation r from the equilibrium bond distance of the molecule. In the lower part, the color code shows the occupation of the adsorbate atomic orbitals, while the contour lines (and numbers) show the potential energy. Reprinted from Reference [39] Copyright (2021), with permission from Elsevier.

solid/liquid interface is a formidable challenge. Hence, the parametrized solvation effects in model Hamiltonians have to be considered with at least as much caution as for DFT-based approaches. Unfortunately, these shortcomings are currently unavoidable.

Ref [43] presents a typical application of this model Hamiltonian to the alkaline Volmer step ($\text{H}_2\text{O} + \text{e}^- + \text{Surf} \longrightarrow \text{H@Surf} + \text{OH}^-$). The model demonstrated that the desolvation of OH^- and the intrinsic energy requirement for breaking the O-H bond in H_2O is responsible for the slow hydrogen evolution reaction (HER) in alkaline compared to acidic conditions.

Other recent applications of model Hamiltonians include the CO_2 reduction reactions on a gold electrode [44], as well as the electrochemical reduction of Ni(II) complexes [45]. They illustrate the insight that can be gained from model Hamiltonians, which continue to be refined [46, 47].

3. Atomistic Models for the Electrocatalytic Interface

Model Hamiltonians discussed in the section above provide an effective (parametrized) description of the free energy surface. In contrast, energies of atomistic models evaluated by DFT provide a first principles description of the electrocatalyst: the precise adsorption mode of complex adsorbates (e.g., glycerol[48]) and the atomic details (defects, co-adsorbates and coverage effects[30, 14]) can be included. Furthermore, the distribution of the electrons within the system is obtained as the result from the self-consistent field process. This means that in the standard constant charge computations the electrochemical potential and the charge transfer from/to adsorbates are a result of the computation. Since electrocatalysis is an inner sphere process, one can assume that the transition state is located at a point where the electrochemically active species is in close contact with the electrode. Therefore, most atomistic studies in heterogeneous electrocatalysis focus on the chemical reaction once the reactants are adsorbed and do not assess the energy required to transport the reactants from the bulk through the electrical double layer to the surface.

3.1. From CHE to Transition States

The computational hydrogen electrode (CHE) model introduced by Norskov and co-workers [12] is, without doubt, the most popular approach in electrocatalysis. CHE adopts a constant charge framework, i.e., the workfunction

is not controlled and might thus change along a reaction coordinate. Furthermore, CHE is mostly applied in the presence of an ice-layer to mimic the solvent or in complete absence of explicit solvent molecules. In its original formulation CHE only applies to thermodynamics, i.e. in the CHE framework the electrochemical potential only affects reaction steps where the stoichiometry of the computed system changes. In other words, the relative energies of adsorbed species only shift as a function of the electrochemical potential when an H atom ($\frac{1}{2}H_2 \rightleftharpoons H^+ + e^-$) is added or removed from the system. Since the stoichiometry cannot change at the transition state, CHE does not affect activation energies.

The determination of activation free energies at constant charge and stoichiometry can still be performed using standard algorithms for identifying the "static" (0 K) TS, to which thermal free energy corrections can be added via statistical mechanics. The free energy difference between the reactant and the transition state corresponds to the activation free energy. This approach for locating TS is well validated at the solid/gas interface, where close agreement with experimental measurements can be obtained.[49, 50] Technically, transition states are usually located by a combination of the nudged elastic band (NEB) [51] and dimer method [52] or applying the climbing image variant of NEB [53]. These methods require about 10^3 energy evaluations in order to locate a TS. The various methods have been efficiently applied in heterogeneous electrocatalysis, such as in the conversion of CO_2 [54], water splitting [55], the oxygen evolution reaction [56] and the hydrogen evolution reaction [57].

In practice, the electroactive species (e.g., $H_3O^+ + e^-$) is placed close to the surface and the transfer of the proton to the surface (or adsorbate) is studied. While still being used in the community (e.g., ref [58]), this approach comes with a major drawback: The effective potential felt by the adsorbates change significantly (up to 2 V) between initial ($H_3O^+ + e^- + Surf$) and final state ($H@Surf + H_2O$) [59]. Hence, such an "initial" state is likely an "artificial" high-energy state compared to having the proton in solution and the electron in the electrode. On the one hand, the solvation of the proton requires a large number of water molecules to be well represented [60], which is not compatible with practical unit-cells. On the other hand, the accompanying electron leads to a large surface charge density and thus to a very negative effective electrode potential [61]. To illustrate how such a model can skew results take, for instance, the case of the reduction of CO_2 to formic acid (see Figure 3): While the TS towards the carboxyl intermediate

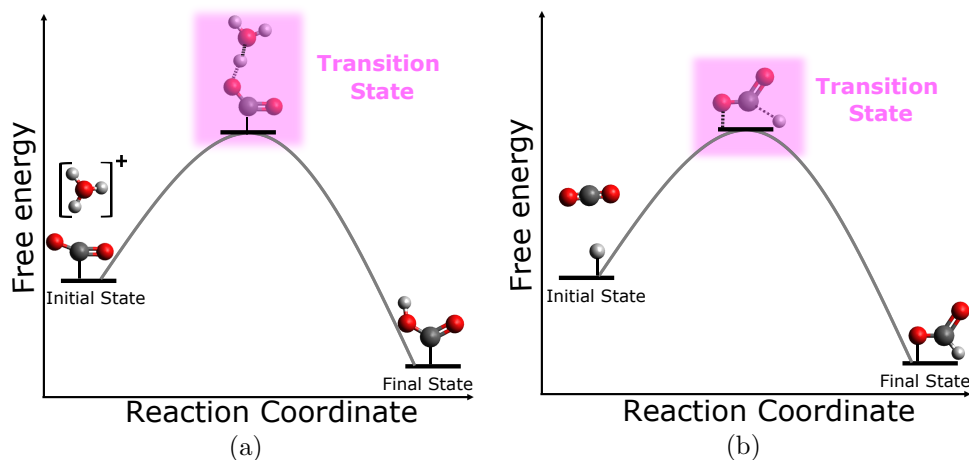


Figure 3: Schematic of (a) an electro-reduction ($\text{H}^+ + \text{e}^-$) and (b) a surface mediated "chemical" reduction leading to two different reaction intermediates (COOH and HCOO, respectively) during CO_2 reduction. While reaction (b) shares common features with heterogeneous catalysis, reaction (a) is typical for electrocatalysis.

(a) might require the intervention of a $\text{H}_3\text{O}^+ + \text{e}^-$ pair and thus all the issues just discussed, the TS leading to the formyl intermediate (b) does not involve such a "charge-separated", high-energy initial state. Hence, one can expect imbalanced accuracy between the two competing reaction paths.

3.2. Cell/Charge Extrapolation Method

In order to overcome the abrupt change in potential during the reaction from the initial state to the TS and then the final state, the generalized CHE method by Norskov and co-workers [62] has been used to extrapolate the results from small and medium sized unit-cells to achieve a constant-potential description, corresponding to the hypothetical infinite size unit cell [63]. In practice, the typical water/proton cluster mentioned in section 3.1 is replaced by an explicit layer of water molecules supplemented by a varying number of H atoms. This makes the method somewhat dependent on the specific structure of the water layer. Furthermore, consistently placing various reaction intermediates and transition states (including of flexible molecules) in an explicit layer of solvent is at best cumbersome, if not impossible, and the situation is even worse if non-aqueous electrolytes are investigated. Last but not least, the model and methodology is computationally very intensive, making it impractical for complex reaction mechanisms.

To address this challenge in a more computationally tractable way, Janik et al. developed a simple approach to evaluate potential-dependent activation barriers of elementary steps in a CHE-like spirit and applied it to the CO₂ electroreduction mechanism on Cu electrodes [64, 65]. The activation energy at 0 V vs RHE is determined at constant (zero) charge, but the barrier is then assumed to have a potential dependence that is proportional to the change in the surface dipole moment between the TS and the initial state (IS). This model is a first order approximation, assuming that the electrostatic interaction between the surface and the electric double layer dominates and that the IS and TS (and thus their dipole moments) do not change as a function of the electrochemical potential.

Subsequently, Norskov et al. proposed a more rigorous, yet almost equally simple method that relies on the change in workfunction between the TS and the IS, combined with an estimate of the effective charge of the corresponding intermediates [66, 67]. The results obtained by this charge extrapolation method for the proof of principle reaction (HER) were shown to agree well with the predictions of the cell extrapolation method.[67] However, the charge extrapolation method depends, by construction, on the scheme applied for determining atomic charges: given that the two popular choices (Bader and Hirshfeld charges) differ up to a factor ten[68] significant differences can be obtained. Nevertheless, well behaved trends have been extracted by this method for proton coupled electron transfer (PCET) reactions.[20] Note, that just like Janik’s model, this charge-extrapolation method assumes that the TS structure does not significantly change as a function of the electrochemical potential.

3.3. Grand-Canonical DFT for Transition States

The charge or cell extrapolation methods described in section 3.2 compute the electrode workfunction but do not control it explicitly. Furthermore, they rely on a constant charge model when searching for transition states. After pioneering work by Liu and co-workers [69] and based on a series of developments of the grand-canonical (GC) DFT approach (see ref [70, 71] for a review), Head-Gordon et al. proposed an elegant way to explicitly control the electrode potential in DFT [72], allowing the search for transition states while maintaining a constant potential at each step along a path with minimal free energy. In this GC-DFT scheme the electrode potential is varied by changing the number of electrons, while the system is solvated and neutralized by the Poisson-Boltzmann equation.[73]

The tremendous advantage of GC-DFT is that it also seamlessly assesses the impact of the electrode potential on formally "chemical" steps, i.e., where the electrochemical couple (typically $\text{H}^+ + \text{e}^-$) is not involved. For example, the activation energies for the C-C bond formation of $\text{CO@Cu}(100)$ show a significant potential dependence (see Figure 4).[72] Intriguingly, these computations predict an unusual behavior: even though the product gets stabilized when moving towards reducing potentials, the transition state gets destabilized. This can be rationalized by electrostatic repulsion between the partially negatively charged reacting CO adsorbates, leading to an "early" transition state. Nevertheless, shortcomings of the implicit solvation model for these charged species cannot be completely excluded at this stage. As a counter example of the potential dependence of this "chemical" step, barriers for some "proton transfer steps" resembling the one of Fig 3b were found to only exhibit a small potential dependence [74], demonstrating that the potential dependence of activation barriers has to be assessed for each type of reaction. The use of GC-DFT for electrocatalytic barriers is now well accepted as illustrated by applications to the HER mechanism on MoS_2 [75] and the electrochemical promotion of catalysis for methane oxidation [76].

The main limitation of GC-DFT is that it introduces all the limitations of using a continuum model for the solvent and electrolyte distribution. [29, 77] These limitations are, however, also intimately connected with the strength of GC-DFT: the use of implicit solvation models, in combination with the rigor of constant-potential computations, is the most practical approach to assess potential dependence of activation barriers for entire reaction networks.

3.4. Fully Explicit Electrocatalytic Interfaces

The previously discussed (also called "static") methods neglect the dynamics of the solvent involved in ion transfer reactions and do not take into account the entropic barriers encountered in electrochemical reactions. In order to identify transition states in the presence of explicit solvents, the "static" NEB/dimer algorithms are no longer applicable: the degrees of freedom of the liquid have to be sampled at the reaction temperature, not optimized at 0 K. Hence, constrained molecular dynamics (CMD), also called "accelerated" or "biased" MD, has to be applied. The most widely used CMDs are thermodynamic integration (TI) [78], Umbrella sampling (US)[79] and metadynamics (MTD)[80]. In CMD the molecular dynamics simulation is performed in presence of either a constraint, strictly imposed via a Lagrange multiplier (TI), or a biasing (Gaussian (MTD) or harmonic (US))

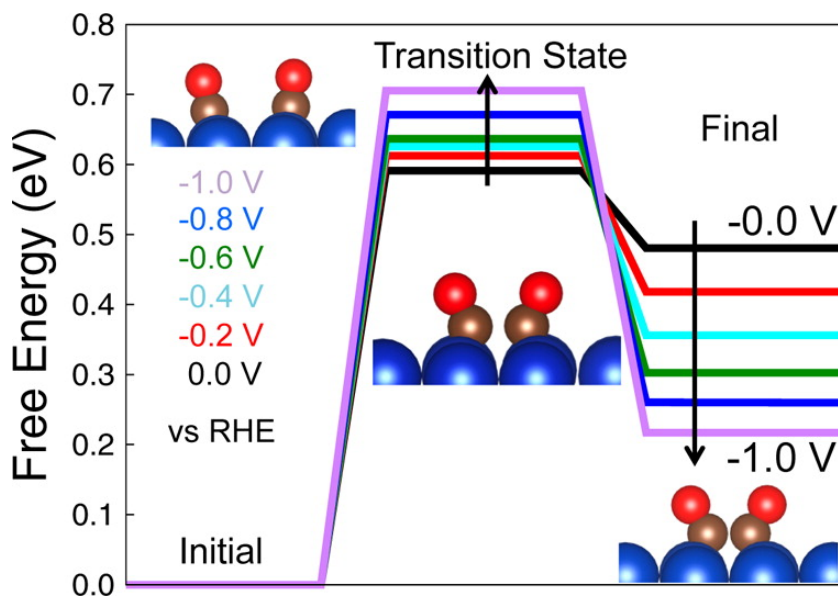


Figure 4: Relative free energy at different potential values of the initial configuration, transition state, and final configuration for formation of CO dimer. Reprinted with permission from [72]. Copyright (2021) American Chemical Society.

potential. This constraint imposes the conversion of the system from the reactants to the products via the transition state.[81] CMD is computationally significantly more expensive than the "static" methods, as they require some $10^4 - 10^5$ of energy evaluations of the interface. The advantage of these dynamic methods is, however, that thermal effects (e.g., surface deformations) are more accurately captured than when optimizing transition states at 0 K.[82] US and TI directly yield a free energy profile, on which the activation energy can be read from the energy difference between the energy at the minimum and the saddle point. MTD generates a free energy surface in a 2 or higher dimensional space, just like model Hamiltonians. Identifying the transition states on these surfaces is then achieved as mentioned in section 2. Goddard and co-workers have shown that entropic corrections can be derived from CMD and metadynamics for fully solvated electrochemical interfaces.[83] Their study featured for the first time a fully explicit electrochemical interface model for a complete electrochemical reaction path. This fully atomistic molecular dynamics description of the interface allowed to uncover the mechanism of CO_2 reduction to methane: the simulations predicted that the so far overlooked CHOH^* intermediate is the branching point

between methanol and methane.[83]

With the ever increasing computational power, CMD has become increasingly popular to investigate the effect of explicit solvent models on electrocatalytic reactions.[84] For example, detailed studies have been performed for the oxygen evolution [78, 85, 56] and NH_3 electro-oxidation [86] reactions.

However, CMD simulations are generally performed in a constant-charge environment (see ref [87] for a noteworthy exception), which means that the barrier determined by this method is not at a fixed workfunction (electrochemical potential). Instead, the charge extrapolation scheme proposed by Nørskov et al. [67] can be applied to correct the potential dependence of the electrochemical barriers.

Overall, CMD is inefficient for simulating a full network of complex reactions. Nevertheless, fully explicit solvation models may be required to discriminate between reaction paths that are as radically different as hydrogenation from H@surf and the electro-hydrogenation via $\text{H}^+ + \text{e}^-$, depicted in Figure 3.

4. Combining Model Hamiltonians with GC-DFT

As discussed in Section 2, model Hamiltonians have transparent interpretations for the described physical/chemical phenomena in the sense that the role of the solvent and adsorbate reorganization can be analyzed separately from the interaction with the electrode and the electron transfer. However, this insight comes at the cost of parameters that are difficult to obtain in a consistent manner. Hence, a sensitivity analysis of the chosen parameters might be required to ensure robust conclusions. In comparison to model Hamiltonians, current DFT methods provide a coherent treatment of the reaction and its environment, but are computationally too expensive. Moreover, dynamically adding/removing counterions to keep the potential constant during a (electro-)chemical transformation is currently unfeasible in DFT, limiting its grand-canonical formulation to implicit solvent/electrolyte descriptions. Recently, Melander and co-workers have proposed to overcome these respective limitations by combining a general rate theory with a Schmickler-Newns-Anderson model Hamiltonian extended to the grand-canonical ensemble [88, 89, 90].

The main strength of Melander’s work is that the potential dependent activation energy is written in terms of a fixed potential reorganization energy, which is analogous to Marcus λ , and a potential-dependent reaction en-

ergy. This is achieved by extending Empirical Valence Bond (EVB) theory to grand-canonical ensembles, called GC-EVB. GC-EVB is illustrated by identifying the transition state geometries for the adiabatic Au-catalyzed acidic Volmer reaction using (constrained) GC-DFT [88]. While the application of this framework might be too cumbersome for routine work, it is sufficiently practical for gaining chemical and electrocatalytical insight for important reactions and rationalizing surprising experimental results. Hence, we foresee a bright future for this or similar approaches, like the independently developed method by Abild-Pedersen and co-workers that is equally EVB-based.[91]

5. Conclusion

The last decade has brought a wide-spread use of thermodynamic DFT descriptions of heterogeneous electrocatalysis. We are convinced that evaluating potential-dependent activation energies constitutes the next step in computational electrocatalyst rationalization and design. Herein, we have reviewed the available methods to evaluate activation energies in heterogeneous electrocatalysis, ranging from model Hamiltonians to standard DFT, GC-DFT and combinations thereof. From our perspective, GC-DFT is the most versatile approach to assess potential-dependent activation energies. However, practically and rigorously combining GC-DFT with explicit solvent/electrolyte simulations remains challenging due to the large number of atoms and extensive phase-space sampling associated with a representative description of solid/liquid interface. Therefore, the area of finding the best compromise between model complexity, predictive accuracy and gained insight will remain active in the foreseeable future.

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