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Title: Electrocatalytic rate constants from DFT simulations and theoretical models : Learning from each other

Year: 2022

Version: Published version

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Please cite the original version:

Domínguez-Flores, F., & Melander, M. M. (2022). Electrocatalytic rate constants from DFT simulations and theoretical models : Learning from each other. *Current Opinion in Electrochemistry*, 36, Article 101110. <https://doi.org/10.1016/j.coelec.2022.101110>



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Review Article

Electrocatalytic rate constants from DFT simulations and theoretical models: Learning from each other

Fabiola Domínguez-Flores and Marko M. Melander

**Abstract**

Electrochemical interfaces present an extraordinarily complex reaction environment, and several, often counter-acting, interactions contribute to rate constants of electrocatalytic reactions. We compile a short review on how electrode potential, solvent, electrolyte, and pH effects on electrocatalytic rates can be understood and modeled using computational and theoretical methods. We address the connections between computational models based on DFT and (semi)analytical model Hamiltonians to extract physical or chemical insights, identify some omissions in present DFT simulation approaches and analytic models, and discuss what and how simulations and models could learn from each other.

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Current Opinion in Electrochemistry 2022, 36:101110

This review comes from a themed issue on **Fundamental & Theoretical Electrochemistry**

Edited by **Rama Kant** and **M.V. Sangaranarayanan**

For a complete overview see the [Issue](#) and the [Editorial](#)

Available online 7 August 2022

<https://doi.org/10.1016/j.coelec.2022.101110>

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Keywords

Solvent, Electrolyte, pH, Electrode potential, Rate constant.

Introduction

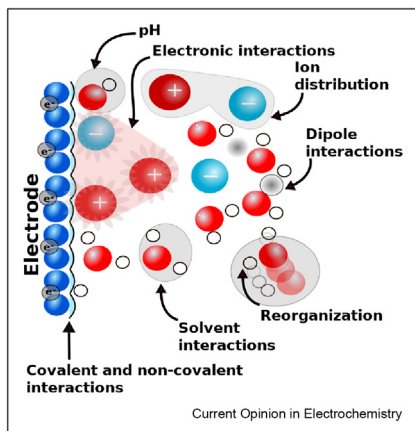
It is becoming increasingly clear that reaction thermodynamics and covalent bonding alone cannot satisfactorily describe electrocatalytic reactions [1,2]. From the DFT modeling perspective, this means that we need to step away from the convenient computational hydrogen electrode model of reaction thermodynamics to modeling reaction kinetics. This needs to be accompanied by the adoption of more comprehensive models of the entire electrochemical interface (ECI) as depicted in [Figure 1](#), where it is not enough to consider

interactions between the adsorbates and the electrode only – we also need to account for the pH, electrolyte, solvent, and electrode effects which are mediated through chemical bonds (covalent, ionic, and metallic) as well as non-bonding or weak interactions, such as electrostatic (field, dipolar, and polarization) and van der Waals interactions between different constituents of the ECI. Attempting to do this with brute-force simulations would be an enormous leap in system complexity and computational cost. Even if such simulations could be performed, it would be difficult to isolate the role of a single specific variable and extract deep understanding of electrocatalytic reactions and their kinetics [3].

The question is then how to develop simulation and theoretical methods capable of separating the impact of different, often coupled, interactions present at ECIs. In our opinion, this requires further development and application of microscopic model Hamiltonian theories based on quantum and statistical mechanics, combining them with explicit atomistic and continuum models of ECIs [4,5]. Although this is not a new idea, recent developments in both semi-analytic theoretical models and DFT simulations have provided crucial insight into how different electrolytes and electrode potentials determine the properties of electrochemical double layers at the atomic scale [5]. For instance, *ab initio* molecular dynamics (AIMD) simulations and careful analysis of the electrolyte at Pt (111) [6] motivated the development [7] of a modified Poisson–Boltzmann (mPB) continuum theory of ECIs. The combination of explicit AIMD simulations and implicit continuum models conclusively demonstrated the importance of water adsorption and non-covalent interactions in defining double-layer capacitance under different electrode potentials and electrolyte conditions. These studies exemplify how tight integration of simulations and theory leads to significant improvements in both and provides insight into double-layer capacitance and structure [5].

Such advances have, however, mainly improved the thermodynamic description of ECIs. The same methods cannot always be directly applied to disentangle the factors determining electrocatalytic rates which is an even more complicated task. Here, we discuss how our understanding of electrocatalytic kinetics can be enhanced by combining semi-analytic model Hamiltonian and DFT simulation approaches.

Figure 1



Depiction of various interactions at ECIS.

We do not focus on computational techniques to model transition state structures and barriers as this area was covered recently [8]. We also limit ourselves to mostly classical adiabatic reactions as nuclear tunneling or non-adiabatic effects in proton-coupled electron transfer (PCET) reactions were reviewed recently [9]. We also limit ourselves to a more general discussion on model Hamiltonians, DFT, and various physicochemical effects rather than specific systems or electrode materials as these have been reviewed recently in the context of electrochemical electron transfer [10]. With these constraints in mind, we aim to provide a perspective on how the interplay between semi-analytical rate theories and atomistic simulations could be strengthened and used to isolate how different factors contribute to electrocatalytic rates.

Exact and semi-analytical microscopic rate theories

Electrocatalytic experiments are usually conducted under the conditions of fixed temperature, electrode potential, and concentration or pressure. It is possible to replicate such conditions in DFT simulations by working in the grand canonical ensemble (GCE) [11] which provides an exact [12] and systematically approximable [13] thermodynamic description of ECIs. The recently developed GCE rate theory [14] similarly provides a formally exact formulation of electrochemical and electrocatalytic rate constants:

$$\begin{aligned}
 k_{GCE}(U) &= \kappa(U) \frac{\Xi^\ddagger(U)}{\Xi^I(U)} = \kappa(U) \frac{1}{\beta\hbar} \exp[-\beta\Omega^\ddagger] \\
 &= \kappa(U) k_{TST}(U)
 \end{aligned}
 \quad (1)$$

where $\beta = 1/k_B T$, and the grand canonical initial (transition) state partition functions Ξ^I (Ξ^\ddagger) depend explicitly on the

electrode potential U . The rate can be written either in terms of the potential-dependent barrier Ω^\ddagger or the transition state theory rate k_{TST} . Note that $\kappa(U)$ accounts for all beyond TST contributions, such as tunneling and solvent dynamics. The GCE rate theory provides a rigorous theoretical background for simulating electrocatalytic rates which for classical adiabatic reactions can now be routinely computed within GCE-TST and GCE-DFT [8].

However, different models and approximations are still necessary to understand how experimentally controllable variables, such as electrode potential, pH, electrolyte, and solvent impact reactions rates at ECIs. Even with the constraint of describing classical adiabatic reaction rates within TST, semi-analytical rate theories are much more complicated than thermodynamic models of ECIs. A rate model needs to include all interactions determining the thermodynamic properties, but simultaneously account for how these interactions vary as a function of the reaction coordinate. To describe all aspects of ECIs presented in Figure 1, a general Hamiltonian needs to encode the impact of electronic structure and interactions (H_{el}), solvent reorganization and interaction with the reactants/products (H_{sol}), bond formation/dissociation (H_{bond}), and non-covalent interactions in double layer (H_{dl}). Such a general model Hamiltonian can be written as [15–19].

$$\begin{aligned}
 H(X, r, R; U) &= H_{el}(r, R) + H_{bond}(X, r, R) + H_{sol}(X, r, R) \\
 &\quad + H_{dl}(X, r, R)
 \end{aligned}
 \quad (2)$$

where X is the solvent reaction coordinate (see Section 4), r is the bond dissociation/formation coordinate, R is the distance between the reactant and surface, and *all* terms depend on the electrode potential U and other reaction conditions. In principle, all terms can be self-consistently included within GCE-TST and DFT but extracting understanding still requires models. Traditional models like the Butler-Volmer [20,21] facilitate the estimation of electrocatalytic kinetics [22,23], but all information is contained in the symmetry factor and exchange current density making it difficult to understand or predict how the rate depends on the different interactions in Eq. (2). Below we discuss chosen examples on how each term affects electrocatalytic rates and how they could be addressed with DFT methods and effective Hamiltonians.

Electronic interactions and electrode potential effects

Electronic interactions between the electrocatalyst and reaction intermediates have been widely studied with direct DFT simulations and model Hamiltonians [10]. These interactions are included in H_{el} which in the simplest case is nothing else than the well-known Newns-Anderson Hamiltonian [24], which provides predictions on how adsorption energies depend on the

electronic structure and coupling strength between different orbitals. In heterogeneous catalysis, H_{el} is often associated with the d-band model [24,25], which has been highly successful in explaining and predicting the reactivity of surfaces. If predictions from the Newns-Anderson model are combined with the Sabatier principle, one can construct Volcano plots describing electrocatalytic activity in terms of binding energies, electronic structures, and orbital-orbital interactions. Such approaches are still *de facto* standard procedure to understand electrocatalysis [26].

One key difference between the electronic interactions as inferred from standard DFT simulations and the models for the H_{el} -term is that the former uses a single adiabatic state, whereas the latter is based on multiple diabatic states. The H_{el} describes the coupling or hybridization of diabatic states through electronic interactions, and one can solve for the adiabatic ground state of the coupled reactant-electrode system [10,9]. The treatment of H_{el} depends on the purpose and the chosen theoretical framework. When working within the Newns-Anderson framework, diabatic states do not need to be specified explicitly, and H_{el} can be obtained through fitting the chemisorption functions to reproduce the adsorbate projected electronic density of states [16]. If a Newns-Anderson-like approach is not used, the diabatic states need to be explicitly specified, and a diabatic Hamiltonian needs to be built and diagonalized to obtain the adiabatic surface. In this case, the electronic part encoded in H_{el} describes the interactions between *a priori* defined diabatic states, and H_{el} can be obtained by fitting a model to reproduce experiments [27], estimated as the difference between the adiabatic and diabatic barriers [14], or computed directly [28]. A good discussion on this topic can be found in a recent review [9]. As discussed in the following sections, the choice between adiabatic or different diabatic descriptions has direct consequences on how the solvent, electrolyte, and pH effects are treated.

However, H_{el} can be used as a direct measure for hybridization and as such it is one of the most important features determining (electro)catalytic properties; without strong hybridization, the barrier can be obtained with first-order perturbation theory resulting in the iconic Marcus theory of Eq. (3), where the electronic interactions are only indirectly present. Hybridization, on the other hand, depends sensitively on the electronic structure and interactions rendering electrocatalysis material and reaction specific. Diabatic states and explicit evaluation of H_{el} appear natural for treating reactions in weakly coupled systems, such as outer-sphere reactions, whereas strongly coupled electrocatalytic inner-sphere reactions are more naturally treated with a single adiabatic state and Newns-Anderson-type models.

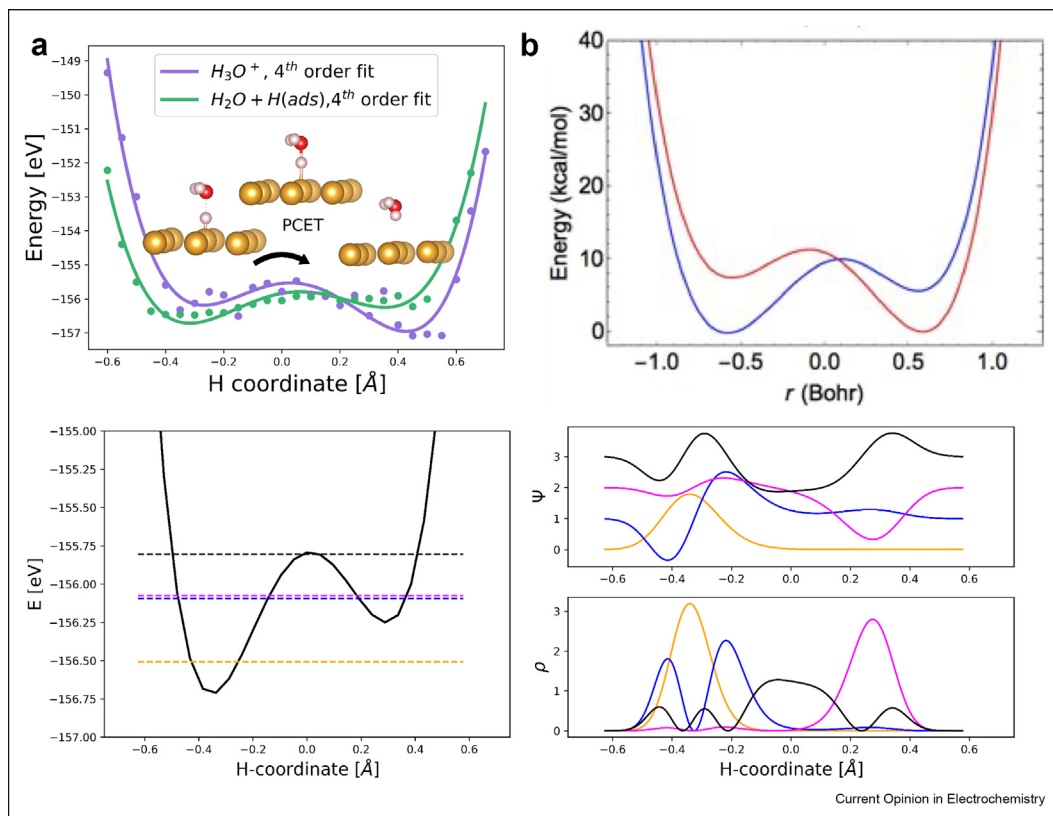
The above explains why DFT is so widely used for simulating electrocatalytic reactions, but studies on outer-sphere reactions are scarce. Even in the rare cases where DFT has been used for simulating outer-sphere reactions, this is done in by coupling DFT directly with the Newns-Anderson Hamiltonian [19,29]. As many electrocatalytic reactions, such O₂ and CO₂ reduction [30,31], are proposed to include outer-sphere electron transfer steps, there is a clear need for quantum mechanical methods and simulations to directly simulate diabatic states and estimate outer-sphere reaction rates.

Not only outer-sphere reactions but also many inner-sphere electrocatalytic reactions are naturally described within a diabatic picture in effective Hamiltonian treatments [9,17,27]. While the computation of diabatic states with DFT at ECIs has not been reported in the literature, this can be achieved with, *e.g.*, constrained DFT (cDFT) [14,32], a widely available method. Figure 2 shows the first example of such calculations. The GCE-cDFT-derived diabatic states for the acidic Volmer reaction on a solvated Au (111) surface compare well with model asymmetric double well diabatic potentials used in Refs. [33,34] to model PCET, but these cDFT calculations self-consistently include electrode surface, electrode potential, and solvent effects. Such diabatic states can be directly coupled with general the PCET theory where proton transfer takes place through tunneling [27,9]. It is important to note that the diabatic DFT calculations predict double-well proton potentials and corresponding wave functions rather than, *e.g.*, simple harmonic or Morse potentials and wave functions commonly used in model treatments.

Even though electronic interactions are extremely important, it needs to be stressed that H_{el} and all properties derived from it are just one component of Eq. (2). If one focuses exclusively on H_{el} , the “only” difference between electrocatalysis and heterogeneous catalysis is the ability to control the Fermi-level or electrode potential to modulate electronic interactions. Usually, the reaction energies and barriers are linear and quadratic functions of the electrode potential, respectively, which is well-understood by theoretical models and simulations. Some materials, such as semiconductor or low-density-of-states electrocatalysts, like graphene, seem to stray away from the linear or quadratic dependencies and exhibit more complex behavior [36]. Nevertheless, even in these cases, the electronic interactions and electrode potential effects can efficiently and explicitly evaluated using GCE-DFT methods [11].

While the electronic interactions between the electrocatalyst and reaction intermediates are quantum mechanical in origin and inherently complex, their impact on electrocatalysis is most often adequately described

Figure 2



Upper left: Diabatic states for the proton transfer in acidic Volmer reaction on Au (111). The proton is scanned at the adiabatic transition state found for the equilibrium potential in Ref. [14]. The calculations are carried out with GCE-constrained DFT by setting the charge +1 on H_3O^+ and charge 0 for $\text{H}_2\text{O} + \text{H}$. Otherwise, the calculation details are the same as in Ref. [14]. Previously, unpublished results. Upper right: The model diabatic states of hydrogen transfer in Ref. [33]. Reproduced from Ref. [33] with permission from the Royal Society of Chemistry. Lower left: The proton vibrational energies (dashed lines) for the $\text{H}_2\text{O} + \text{H}(\text{ads})$ structure obtained by solving the Schrödinger equation for the proton in $\text{H}_2\text{O} + \text{H}(\text{ads})$ diabatic potential. The Schrödinger equation was solved with the Fourier grid method [35]. Lower right: The proton wave functions (Ψ) and densities (ρ) are for the wave for the $\text{H}_2\text{O} + \text{H}(\text{ads})$ diabatic potential.

by the Newns-Anderson model and (GCE-)DFT simulations, even if quantitative accuracy is difficult to obtain. The major outstanding problem is the simulation of outer-sphere reactions which call for development and utilization of diabatic electronic structure methods. Yet for most cases relevant to electrocatalysis, it seems fair to say that the electronic interactions and electrode potential effects can be addressed and understood both with semi-analytical models and DFT simulations.

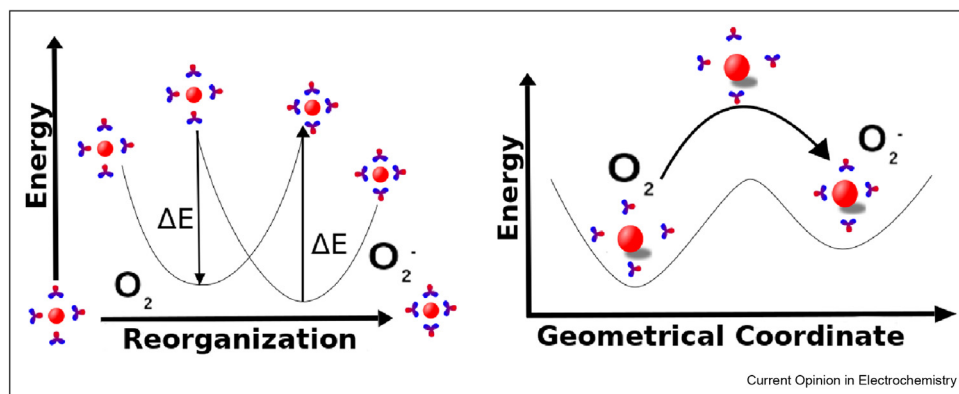
Solvent effects

Electrocatalytic reactions take place at solid–liquid interface which directly indicates that both the solid and liquid components need to be handled with equal care. Yet most focus from simulations and semi-analytical models has been directed toward understanding the influence of the solid component and electronic, quantum mechanical interactions. Even though the liquid is adequately modeled using a classical description, the theoretical treatment of (inhomogeneous) liquids is very

complicated, and several approaches have been put forth [37].

In electrocatalytic rate theories, the solvent has a very special role as solvent reorganization defines the reaction coordinate X . This means that the reaction coordinate includes at least one collective (solvent) property, which comes in variety disguises, such as solvent reorganization, rotation of solvent dipoles, or energy gap, between the initial and final states. All rate theories where the term “solvent reorganization” appears are based on the picture where electrocatalytic reactions are driven by the solvent. Such theories emphasize the importance of solvent fluctuations, dipolar reorganization, and their active role in initiating and completing the reaction. On the contrary, most DFT simulations treat the solvent as a passive component adapting to the changes brought about by bond formation/breaking and in stabilizing reacting species. This view is directly reflected on the choice of a reaction

Figure 3



Left: Depiction of dipolar solvent reorganization around an oxygen molecule during outer-sphere electron transfer treated within the Marcus picture. Note that the solvent structure is the same for both states at each reorganization coordinate value. Right: Depiction of smooth solvent reorganization during an adiabatic reaction modeled using standard transition state theory.

coordinate as atomic simulations typically treat geometric variables [8], such as bond lengths or angles, as reaction coordinates.

As depicted in Figure 3, these opposing views on the reaction coordinate and solvent effects directly reflect on how the solvent is treated in DFT simulations and model Hamiltonians. DFT simulations attempt to directly evaluate either the partition functions or the barrier in Eq. (1), whereas the semi-analytic rate theories obtained with model Hamiltonians typically express the rate as a function of solvent reorganization coordinate and energy.¹ The seminal Marcus theory of electron transfer provides a prime example

$$k_{\text{Marcus}}(U) = \frac{1}{\beta\hbar} \exp \left[-\beta \frac{(\lambda(U) + \Delta G(U))^2}{4\lambda(U)} \right] \quad (3)$$

where both the solvent reorganization energy λ and reaction energy ΔG in general depend on the electrode potential [14,38]. Equation (3) directly shows that potential-dependent solvent properties are an integral part of electrocatalysis, and solvent contributions cannot be separated from electrocatalysis — they are at par with electronic interactions. Similar arguments can be made for theories of PCET and ion-coupled electron transfer (ICET) reactions treated below.

At this instance, it needs to be stressed that Eqs. (1)–(3) do not depend on time or any dynamical effects (apart from κ): only time-independent, equilibrium, or non-equilibrium *thermodynamic* quantities enter these equations. Effects such as solvent reorganization dynamics or collision time scales do not impact TST-based

rate constants or Marcus theory even when advanced sampling techniques such as thermodynamic integration with constrained *ab initio* molecular dynamics (TI + cAIMD) are used. “only” time-independent partition to evaluate TST rates in Eqs. (1)–(3), “the dynamic sampling of the solvent structure where each point along the reaction coordinate is treated independently” [39] and cannot be considered a limitation of TI + cAIMD or any other computational method discussed herein. Dynamic or time-dependent solvent sampling is not even needed for the evaluation of rates within GCE-TST, and the same information is in principle available from implicit solvent or explicit Monte Carlo simulations. What is needed is a statistical treatment rather than static solvent molecules or ice [40] and the inclusion of structural fluctuations [41]. The statistical averaging can be performed either after a simulation, as done in AIMD or Monte Carlo techniques, or *before* the simulation, as in implicit or continuum solvent models based on statistical liquid theories [37].

The computational realizations of statistical averaging differ depending on whether the Marcus (Eq. (3)) or TST picture (Eq. (1)) is used. In the TST picture only equilibrium, *i.e.*, adiabatic solvent models are needed as the solvent structure adapts smoothly to the variation of the geometric coordinates as shown in Figure 3. In this case, all common dielectric, classical solvent models and AIMD techniques are in principle adequate. Marcus-type models require the use of a non-equilibrium solvent model (1) to capture the Franck-Condon-like change in electron/proton localization but without changing the solvent structure and (2) to compute reorganization energy which is an excited state quantity. This leads to the separation of solvent response to “slow” and “fast” modes. The fast modes represent the electronic response which is always in equilibrium with

¹ Electronic interactions of course also included in the model Hamiltonian treatment, see Eq. (2).

the charge, whereas the slow modes correspond to nuclear reorganization, such as dipole rotation, which is out-of-equilibrium when the charge is suddenly altered, see Figure 3. The separation between slow and fast modes requires some advanced simulation methods. At the AIMD level, this can be achieved through coupling a diabatic method, such as cDFT [32,14], with normal MD simulations [42]. With implicit models, this separation has been achieved for molecular systems within the dielectric continuum [43], molecular DFT (mDFT) [44], and the reference interactions site methods (RISM).² [45] However, in solid-state or periodic DFT codes typically used for modeling electrocatalytic reactions, these non-equilibrium implicit solvent models are not yet available.

AIMD simulations can explicitly capture the solvent effects, but this comes with high cost and long simulation times making the study of reactions quite troublesome. Yet, it is not always guaranteed that even extensive AIMD simulations present the thermodynamic state of a system correctly [46]. Implicit solvent models, such as RISM and mDFT, are inherently thermodynamic and appear very promising when properly parametrized [47]. Dielectric continuum models are now widely available in DFT codes [48] but have a bad reputation in modeling electrocatalytic reactions accurately [49]. This reputation is likely at least partially related to the currently available models and their scope. For instance, none of the current dielectric continuum models have been parametrized for interfacial systems. Also going beyond linear dielectric models and accounting for, *e.g.*, dipolar response [50] is expected to be important for capturing interfacial quantities, such as capacitance [51]. Dipolar models are also a faithful, molecular presentation [52] of non-equilibrium solvation and reorganization [52]. Finally, the dipolar models have already been successfully used with effective Hamiltonians [17].

Electrolyte effects

Electrolyte effects in electrocatalysis are a long-standing issue that has recently gathered substantial interest [53,3]. The current understanding is that ions impact electrostatics by modifying non-covalent electrolyte-mediated interactions, poisoning the surface, stabilizing adsorbates, modulating the interfacial pH, and/or changing the solvent structure. All these effects have been considered at DFT [3,54,55] and model Hamiltonian levels [17,56,57,19], but comprehensive understanding has not been achieved: it seems fair to say specific ion effects in electrocatalysis remain currently unresolved. Future work should focus on developing physically and chemically motivated ranking or

classification schemes for specific ion effects in electrocatalytic systems, ideally leading to an electrocatalytic equivalent of the famous Hofmeister series which predicts specific ion effects for a wide variety of chemically and physically distinct systems [58].

The rudimentary models of electrolytes and ECIs are based on the Poisson–Boltzmann equation which shows that ion profile near the electrode interface depends on electrostatic interactions, as well as temperature and entropy (through the Boltzmann factor). It also tells that electrolyte effects cannot be understood without proper thermodynamic averaging. Direct support for this comes from AIMD simulations which have revealed that energy-entropy competition is crucial for understanding ECIs [59]. Unfortunately, achieving proper sampling with AIMD is very difficult, and often very short sampling times are used [55,54], which may result in an incorrect thermodynamic picture of the ion effects [46]. Implicit or continuum electrolyte models directly capture the energy-entropy competition making them not only computationally but also conceptually appealing.

The problem of electrolyte effects in electrocatalytic kinetics can be formulated as an ICET [56,57] or as an ion-influenced PCET [17] reaction. The distinction between ICET and ion-influenced PCET is somewhat arbitrary, but in the former, the reactant molecule interacts strongly with the ion, similar to an ion pair [56,57], and ions are coupled with the solvent reorganization [56], whereas in the latter, the interactions are more indirect influencing the reaction through mean-field electrostatics or by changing the ECI structure [17,19]. Mean-field interactions can be captured with Poisson–Boltzmann-like models, but describing ion pair formation requires either direct simulations or an additional term in the model Hamiltonian [56]. Electrolyte-induced changes in electrostatic and covalent interactions and solvent properties alter reaction free energies, solvent reorganization energies, and consequently the reaction rate.

DFT simulations on electrolyte effects at the AIMD or implicit levels have almost exclusively focused on studying how the ion impact reaction energies, and only few studies have addressed reaction kinetics. Studies on reaction thermodynamics have attributed ion effects to dipole-field or mean-field electrostatics [3] as well as direct ion-reactant pairing through Coulomb interactions [55,54,60]. Few studies on reaction kinetics through AIMD have shown that cations can have a dramatic effect on reaction barriers [61] and even promote an outer-sphere electron transfer pathway [31]. Yet, improved chemical and physical models are crucially needed to understand the underlying reasons for specific ion effects. Without models on ion-dependent solvent reorganization, desolvation, electrostatic interactions, ion-reactant pairing, *etc.*, we cannot predict

² mDFT and RISM are based on molecular models but are still considered implicit models because the explicit solvent molecules are not present and because thermodynamic properties are obtained without explicit solvent sampling.

which of these factors are important or rationally tailor electrolytes enhancing electrocatalytic activity and selectivity.

This is where effective Hamiltonians and continuum models combined with DFT could bring significant understanding and help disentangling different contributions. First, all electrolyte effects discussed above are strictly classical in nature and should be well described using classical or implicit electrolyte models without considering electronic structure of ions [62,40]. The classical nature of ions is suitable for describing the Hofmeister series for a wide range of systems [58]. Implicit models provide a classical, inherently thermodynamic description and can be systematically improved through, *e.g.*, field theoretical techniques [63,64] or by using classical DFT methods [62] which allow the inclusion of different effects such as ion size or excluded volume effects, polarization, desolvation, ion self-energy, etc. None of these interactions have been included in continuum electrolyte models available in DFT codes. Yet, it is known that already the simplest molecular continuum electrolyte model, the dipolar Poisson–Boltzmann model, taking into account solvent dipoles and ion size effects can successfully explain cation over-crowding effects in the oxygen evolution kinetics [65] or electrolyte effects in hydrogen electrocatalysis at the model Hamiltonian level [17]. The dipolar mPB model also captures the solvation energy of simple ions [50], yields a reliable description of interfacial capacitance for simple ECIs [51], and has been extended to treat non-equilibrium electrolyte solvation [66] to study electrocatalytic rates within the Marcus (Eq. (3)) picture. Beyond dielectric models also the RISM + DFT approach can capture specific ion effects without AIMD sampling [67]. Finally, it needs to be emphasized that implicit electrolyte models are in theory and practice and ideally suited for modeling constant potential conditions within GCE-DFT [8,12,5] even though explicit solvent GCE-DFT is also possible [68].

It needs to be reiterated that all electrolyte models discussed in the previous paragraph are both classical and implicit. Yet, these models can describe most, if not all, electrolyte effects proposed in the recent literature, which demonstrates that even relatively simple implicit electrolyte models can capture the essence of the chemistry and physics behind specific electrolyte effects. Furthermore, implicit electrolyte models enable systematic testing and elimination of different interactions in DFT simulations or DFT-parameterized effective model Hamiltonian studies — this would be difficult or even impossible with AIMD simulations. Yet, current continuum electrolyte models available in different electronic DFT codes [48] have a seemingly bad reputation in modeling electrolyte effects [49], but it needs to be emphasized that this view is largely based on the

shortcomings of the simplest linear dielectric continuum model and (linearized) Poisson–Boltzmann model. The performance of DFT combined with more advanced, molecularly-motivated implicit electrolyte models remains an open question. But given the classical nature of ion interactions and systematic improvements in implicit electrolyte models, understanding electrolyte effects could be significantly advanced by implementing and applying advanced implicit electrolyte models in direct DFT calculations or model parametrization.

pH effects

pH effects can be seen as a subset of electrolyte effects and majority of the arguments on modeling electrolytes hold for the pH as well. There are, however, some features that set pH apart from other electrolyte effects. The biggest difference is that pH can change the proton donor [69] from say an H_3O^+ to a H_2O which modifies the H_{bond} -term in Eq. (2) [17]. This effect can be accurately captured with DFT or (quantitatively) approximated with effective Hamiltonians [17]. A more deeply rooted conceptual and theoretical issue with pH is its effect on modeling PCET reactions: while larger ions can be treated classically, proton transfer in general requires a quantum mechanical treatment [9]. Modeling the complications of PCET deserves its own review [9], and here, it suffices to say that the necessity to account for quantum effects requires significant modifications to both model Hamiltonian [4,9,70] and the DFT models [71,4].

Besides quantum effects in PCET, another pH effect not listed in Ref. [69] is the question of how solvated H^+ or OH^- change the properties of interfacial water. Since water reorganization energies depend on the pH [72] and because water is both the solvent and a hydrogen-bond donor/acceptor [73], the pH-dependent water structure is a fundamental part electrocatalysis [1,74]. While pH effects on thermodynamics and reaction barriers within TST picture and geometric reaction coordinates have been considered, these are not enough to explain the pH dependency of reaction kinetics [72,2,74,1] calling for a more comprehensive understanding of pH effects on solvent properties, the reorganization energy in particular. A prime example is the hydrogen electrocatalysis and the role of potential- and pH-dependent “solvent dynamics” [1,2,75]. The term “solvent dynamics” is somewhat misleading as the actual proposed effect is more related to water reorganization energy and the reaction barrier [1] rather than friction-like solvation dynamics [76]. A model Hamiltonian approach has already shown that increasing rigidity of the reaction environment increases the reaction barrier or reorganization energy thus impeding the reaction [17]. But even more generally, DFT models and effective Hamiltonians within the diabatic frameworks (Eq. (2)&(3)) offer a direct way to interrogate pH-dependency in solvent reorganization and appear natural for addressing how pH

affects solvent reorganization and electrocatalysis. At the DFT level, this can be realized through the recent diabatic GCE-EVB theory [14,11] or by extending the diabatic model in Ref. [41] to account for solvent reorganization. These diabatic methods also offer a natural way to parametrize model Hamiltonians for ECIs through GCE-DFT [11,19].

Towards quantitatively accurate model Hamiltonians

Effective Hamiltonians have provided unparalleled qualitative understanding on different interactions and their impact on electrocatalytic rates. Quantitative model Hamiltonians could give even more. Besides deep fundamental understanding, quantitatively accurate Hamiltonians can provide a physically informed approach to catalyst screening in the form of surrogate model used in high-throughput [77] studies. This has already been achieved for the electronic interactions where advances in machine learning methods can be leveraged to describe electronic interactions within model Hamiltonians in catalyst screening [78]. But as discussed throughout this work, electronic interactions are just one component of Eq. (2), and the other terms need to be captured with equal accuracy [11]. The H_{bond} term is naturally described with DFT using adiabatic or emerging diabatic models (Figure 2). If nothing else, the self-consistently computed diabatic bond breaking energies, such as presented in Figure 2, offer a crucial benchmark for the bond potentials and electronic coupling constants used in effective models.

Using effective Hamiltonians in fundamental or screening studies requires further advances in diabatic GCE-DFT methods and solvent/electrolyte models as has been discussed above: we need to shift the focus from the electrode to the entire ECI as depicted in Figure 1. This needs better models for the H_{sol} and H_{dl} terms. As a concrete example, based on the insight from direct GCE-DFT simulations, we recently [19] extended the Newns-Anderson-Schmickler model [15] by including electrostatic interactions formally in H_{dl} . This simple extension facilitated the inclusion of electrostatic interactions in the double-layer, which were found crucial in explaining the outer-sphere electron transfer kinetics through experiments, theory, and simulations with quantitative accuracy. Another particular example is the alkaline hydrogen evolution where either re-parametrization of the effective electrolyte–OH interaction [17] and/or finding a more physically motivated expression for this term through self-consistent DFT calculations could contribute to understanding the pH effects. It also needs to be re-emphasized that all effective interactions potentially depend on the electrode

potential which is captured with GCE-DFT but not yet considered with model Hamiltonian methods.

Conclusions and outlook

We have provided an overview on modeling electrocatalytic rate constants with DFT and model Hamiltonian methods. While DFT approaches can now explicitly include the electrode potential, explicit solvent, pH, electrolyte effects, model reaction kinetics, etc., extracting understanding from direct simulations still requires the use of models, and effective Hamiltonian approaches present the most comprehensive alternative for this. Therefore, we have focused on the differences and similarities between these two approaches to identify common ground and aspects where both could be merged or improved by learning from each other.

One of the main outcomes of this review is the prospects of using electronically diabatic DFT methods and Marcus-like theories. These approaches have the potential to provide a fully atomistic, first principles way to directly probe solvent, electrolyte, and pH effects as a function of the electrode potential. The diabatic DFT descriptions are also more compatible with the model Hamiltonian formulations paving the way for merging the insight from these two methods. By improving the solvent/electrolyte models used with (diabatic) DFT methods, the parameters entering the effective Hamiltonians can be self-consistently computed. Not only the parameters but also the functional forms of effective interactions could be improved with diabatic DFT simulations. For instance, the solvent reorganization and reaction energies could include non-linear dependencies, the functional forms of ion-reactant interactions could be resolved, and the diabatic PCET curves can be computed at ECIs as a function of the electrode potential; this was exemplified with the construction of the first electrode potential and solvent dependent diabatic potentials with GCE-cDFT. To combine diabatic DFT methods with effective Hamiltonians, more development work is still required, and in particular, non-equilibrium continuum models in DFT codes are needed.

While solvent, pH, and electrolyte effects can in principle be accurately described with AIMD, this becomes prohibitive in practice: sampling, e.g., pH = 3 conditions or low electrolyte concentrations would require thermodynamic sampling of thousands of water molecules for extended periods of time. This would be very difficult even with DFT-parametrized machine learning potentials. In this respect, improved implicit models have their own strengths and significant untapped potential. Besides naturally working with GCE-DFT methods, they enable efficient testing and inclusion of different solvent, pH, and electrolyte effects under thermodynamic

equilibrium without explicit sampling. However, extracting even qualitative understanding from implicit solvent/electrolyte models requires parametrization and further development and implementation of more advanced continuum models. Future works should focus on including, *e.g.*, non-linear dipolar solvent, excluded volume, ion size and polarizability, ion self-energy, etc., effects in continuum solvent/electrolyte available in periodic DFT codes.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Marko M. Melander reports financial support was provided by Academy of Finland.

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by the Academy of Finland through the CompEl project (#338228). We also thank Professor Wolfgang Schmickler for his feedback and comments.

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