Grand canonical rate theory for electrochemical and electrocatalytic systems I: General formulation and proton-coupled electron transfer reactions

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A generally valid rate theory at fixed potentials is developed to treat electrochemical and electrocatalytic potential-dependent electron, proton, and proton-coupled electron reactions. Both classical and quantum reactions are treated. The applicability and new information obtained from the theory is demonstrated for the gold catalyzed acidic Volmer reaction.

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Grand canonical rate theory for electrochemical and electrocatalytic systems I: General formulation and proton-coupled electron transfer reactions

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Abstract. Reactions at electrochemical interfaces present a serious challenge for atomistic modelling. While electrochemical thermodynamics are naturally addressed within the grand canonical ensemble (GCE), a fixed potential rate theory is lacking. This omission significantly impedes fundamental understanding and computational studies of electrochemical rate constants. Herein, a generally valid electrochemical rate theory is achieved by extending equilibrium canonical rate theory to the GCE. It is shown that all classical and quantum rate theories can be also utilized within GCE. The extension provides a theoretically rigorous framework for addressing classical reactions, nuclear tunneling and other quantum effects, non-adiabaticity etc. from a single unified theoretical framework. The rate expressions can be self-consistently parametrized with GCE ab initio methods. These features enable well-defined first principles route to reaction barriers and prefactors to treat inner-sphere and outer-sphere reactions as well as electron/proton tunneling in (proton-coupled) electron transfer reactions at constant electrode potentials. GCE barriers and prefactors are derived for i) classical transition state theory, ii) Marcus-like adiabatic curve-crossing picture empirical valence bond theory (GCE-EVB), and iii) quantum treatment for (non-)adiabatic electron and proton-coupled electron transfer reactions. From GCE-EVB generalized free energy relations for electrochemical systems are derived. Utility of the theory is demonstrated by predicting PCET rates and transition state geometries for the adiabatic Au-catalyzed acidic Volmer reaction using (constrained) GCE-DFT. The work herein provides a rigorous theoretical basis and practical computational approaches to electrochemical rates with numerous applications in material screening, and physical and computational electrochemistry.

Keywords: electrochemical kinetics, grand canonical, free energy relations, Volmer reaction, constrained DFT
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1. Introduction

Electrochemical reactions and especially electrocatalysis are at the forefront of current green technologies tackling climate change. To realize and utilize the full potential of electrocatalysis, selective and active catalysts are needed for various applications and reactions including e.g., oxygen and hydrogen reduction/evolution reactions, nitrogen reduction to ammonia and CO$_2$ reduction.[1] These and other electrocatalytic/electrochemical reactions are based on successive proton-coupled electron transfer (PCET), electron transfer (ET), and proton transfer (PT) reactions; the unique aspect of electrochemistry is the ability to directly control PCET, ET, and PT kinetics and thermodynamics by the electrode potential.[2]

Besides the catalyst material, electrocatalytic performance is controlled by the electrolyte composition and electrode potential. To translate these to microscopic, computationally treatable quantities, it is the combination of the electrolyte and electron electrochemical potentials which determine and control the (thermodynamic) state of electrochemical systems. Therefore, an atomic-level computational model needs to provide an explicit control and description of these chemical potentials as depicted in Figure 1. In thermodynamics fixing the chemical potentials is achieved through a Legendre transformation from a canonical ensemble to a grand-canonical ensemble (GCE) for both electrons and nuclei.[3] This calls for theoretical and computational methods for treating systems in which particle numbers are allowed to fluctuate and chemical potentials are fixed.

The theoretical basis for fixed potential electronic structure calculations was developed by Mermin who formulated electronic density functional theory (DFT) within GCE.[4, 5]. Later, GCE-DFT has been generalized for treating nuclear species either classically or quantum mechanically [3, 6, 7, 8, 9]. GCE-DFT provides a fully DFT, atomistic approach for computing free energies of electrochemical and electrocatalytic systems at fixed electrode and ionic/nuclear chemical potentials.[3] Importantly, the free energy from a GCE-DFT calculation is in theory exact and unique to a given external potential. In practice, the (exchange-)correlation effects in both quantum and classical systems need to be approximated. The thermodynamic GCE framework has already been adopted by the electronic structure community to model electrocatalytic thermodynamics at fixed electrode[10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 3] and ion potentials[3, 14, 12]. Based on the large number of theoretical and computational works utilizing GCE-DFT, the computational framework for thermodynamics within GCE seems generally accepted. The thermodynamic approach has provided fundamental atomic level insight on reactions at complex electrochemical interfaces and enabled computational catalyst screening using free energy relations, Volcano curves, and scaling relations.[1]

However, it has been shown that a purely thermodynamic perspective on electrocatalysis is not sufficient for understanding and predicting activity, selectivity, or catalytic trends.[21, 22, 23, 24] Besides applications in catalysis and material science,
electrochemical kinetics are fundamentally important and provide a way to understand complex solvent effects, electron and nuclear tunneling, and non-adiabatic reactions. Ideally both fundamental and applied kinetic computational/theoretical studies should make use of general and self-consistent first principles Hamiltonians within GCE. This has, unfortunately, remained unattainable due theoretical and methodological difficulties and omissions.[25] Surprisingly, a general GCE rate theory has not yet been established; mending this deficiency is the central goal of the present work.

Before diving to the development of the GCE rate theory, it is worth considering what new and important information can be obtained from a general electrochemical rate theory. First and foremost, the theory needs to accurately capture the intricacies of ET, PT, and PCET reactions as function of the electrode potential. Therefore, a general treatment of electrochemical reaction rates needs to be applicable to 1) both inner-sphere and adiabatic as well as outer-sphere and non-adiabatic reactions, 2) sequential ET/PT or decoupled reactions as well as simultaneous PCET reactions, 3) tunneling of both electrons and nuclei, and 4) use with general first principles Hamiltonians within GCE. The motivation to include each of these four requirements are discussed next.

First, adiabatic inner-sphere reactions present a large and important class of electrocatalytic reactions as demonstrated by a large body of computational works aiming to evaluate rate constants for this class of reactions[11, 12, 20, 19, 21, 26, 27, 28, 29, 30, 31, 32]. However important adiabatic reactions are, all electrochemical reactions are certainly not inner-sphere nor adiabatic. In particular, both vibronic and electronic non-adiabatic effects are frequently encountered in outer-sphere and long-range ET, PT, and PCET reactions.[25, 33] Even for electrocatalytic reactions, non-adiabaticity may be present and the importance and contribution of non-adiabaticity may depend on the electrode potential.[34, 35] As a concrete example, it has been shown that only the inclusion of vibronic non-adiabaticity in electrochemical hydrogen evolution reaction can explain experimentally observed Tafel slopes and kinetic isotope effects.[34]
Second, there are several reactions where the PT and ET are decoupled for kinetic reasons. For example, in alkaline ORR pure ET has been proposed as the rate determining step\[36, 37, 38, 39\]. Recent experiments of ORR on carbon-based materials conclusively demonstrate that ET is the rate- and potential-determining step\[40, 41\]. Also solution pH can alter the reaction mechanism and e.g. CO$_2$ reduction can proceed through simultaneous PCET in acidic and through decoupled PCET (ET-PT) in alkaline solutions\[42, 43\]. In general, decoupled ET and PT are expected to play an important role on weakly bonding electrode surfaces in oxygen, CO$_2$, CO, alcohol etc. reduction reactions.\[44\] In such reaction-catalyst combinations long-range ET/PT may take place warranting the inclusion non-adiabaticity effects. From an applied perspective, decoupled steps may enable circumvention of thermodynamic scaling relations and lead to identification of novel electrocatalysts.\[45\]

Third, ET, PT, and PCET include the transfer of very light particles and therefore quantum effects may be very important. Especially nuclear tunneling has a long tradition in electrochemistry\[46\] and experiments have conclusively demonstrated that room-temperature hydrogen tunneling takes place during ORR on Pt, and at low over-potentials tunneling is the prevalent reaction pathway.\[47\] Tunneling contributions are rarely considered in the field of computational electrocatalysis which is mainly due to tradition and methodological difficulties; the computational electrochemistry community has adopted tools and classical transition state theory (TST) from computational heterogenous catalysis where reactions take place at high temperatures and quantum effects are considered negligible. On the other hand, the theoretical electrochemistry community has traditionally considered ET, PT, and PCET in the non-adiabatic, tunneling framework\[36, 48, 49, 50, 51, 52, 53, 34, 54, 55, 56, 57, 58, 59, 60, 61, 62\]. The computational community has been slow in adopting the language and approaches developed by theoretical community which has resulted scarcity of first principles study of tunneling in electrochemical environments.

Fourth, theoretical electrochemistry has long tradition of using model Hamiltonian formulations to understand reaction kinetics. For instance, Marcus\[62\], Dogonadze-Kutzetnotsov-Levich\[48, 49\], Schmickler-Newns-Anderson\[63, 64\], or Soudackov-Hammes-Schiffer\[33, 34, 53, 60, 61, 65\] theories have provided the basis for understanding electrochemical kinetics. The main drawback of these methods is that they require effective parameters obtained from either experiments, simple DFT calculations, or a mixture of these. However, widely different parametrizations for the same reaction can result in similar rates. For instance, differences as larges as $\sim$ 3-4 eV in reorganization energy and the coupling matrix elements\[66, 67, 35, 68\] lead to practically identical reaction rates; it is clear that some unphysical error or parameter cancellation takes place. The difficulty of parameter estimation and error cancellation limits the physical/chemical insight obtained from model Hamiltonians. Furthermore, model Hamiltonians are static and (usually) not self-consistent. Typically, the electrode potential serves to role of changing the Fermi-level in an otherwise static electronic structure. Even when potential-dependent electrostatic interactions and work terms are
included [35, 51, 67, 69], most parameters such as the solvent reorganization energy, chemical bonding characterized by Morse potentials, electrode structure, tunneling matrix elements etc. remain unchanged by the electrode potential. As such, it is unlikely that model Hamiltonians can quantitatively capture the complexity of electrochemical reactions. Besides issues related to self-consistency, model Hamiltonians studies of non-adiabatic reactions implicitly rely on the single orbital picture which is highly problematic for first principles Hamiltonians as discussed in the Supporting Information. Instead, modern fixed potential first-principles methods explicitly incorporate the effect of electrode potentials on the interfacial properties and bonding. Especially the GCE-DFT has proven to provide a well balanced and rigorous description electrochemical interfaces. However, using general first principles methods for addressing ET/PCET kinetics in general have remained largely elusive thus far.

The above discussion highlights how different reactions and phenomena have been and can be addressed in the theoretical and computational communities. Computational works utilize high-quality \textit{ab initio} Hamiltonians but rate constants are based on tools derived from heterogeneous catalysis and electrocatalytic reactions have been studied only using classical adiabatic TST theory. These computational studies describe the electrochemical interfaces in a self-consistent way and there is no need for empirical parametrization of the TST rate equation. Thus far, these methods have only given access to the reaction barrier but not the prefactor beyond the TST approximation. Estimates on importance of the prefactor has relied on perturbative rate theories with model Hamiltonians at the non-adiabatic limit to describe electron/proton tunneling. Other theoretical works extend the Newns-Anderson-Schmickler model Hamiltonian to study both classical adiabatic TST and non-adiabatic tunneling reactions. While both barriers and prefactor have been computed, the models are evaluated using non-self-consistent parametrization. Therefore researchers have been be faced with a difficult choice: Should the study include all the complexity addressed in a self-consistent manner using an \textit{ab initio} approach but with the restriction of classical TST approximation without general prefactors? Or should the studies include prefactors to reflect non-adiabaticity or tunneling but with a empirically-parametrized model Hamiltonian?

In this work this difficulty is resolved by developing a generally valid electrochemical rate theory which can be directly combined with fixed-potential \textit{ab initio} methods. This is achieved by deriving a grand canonical rate theory which builds on Miller’s general equilibrium (micro)canonical rate theory [70, 71, 72]. As Miller’s theoretical framework is equally valid for adiabatic and non-adiabatic as well as quantum, semiclassical, and classical rate expressions[73] and can utilize both model or first principles Hamiltonians[33, 57, 58, 59, 60, 61, 74, 75] the presented novel GCE extension provides a generally valid electrochemical rate theory; the developed GCE rate theory enables using all canonical rate theories in constant potential simulations. In particular, the work herein provides a unified rate theory for computing reaction barriers as well as the prefactors making the theory applicable to treat adiabatic and non-adiabatic reactions, classical and tunneling reactions, and PT, ET, and PCET on equal footing.
using GCE-DFT methods.

Besides developing a general and exact GCE rate theory, approximate techniques for both adiabatic and non-adiabatic reactions are developed. First, for adiabatic ET, PT and PCET reactions a generalized GCE transition state theory (TST) is derived. Second, adiabatic and non-adiabatic Marcus-like empirical valence bond theories (GCE-EVB) are developed. These lead to well-defined (linear) free energy relationships ideally suited for materials’ screening purposes with kinetic information as demonstrated for the acidic Volmer reaction on Au(111) in Section 5. Third, prefactors and quantum mechanical rate constants for electron and nuclear tunneling are derived for ET and PCET reactions using an extended golden-rule formalism within GCE. The golden-rule formalism is ideal for obtaining deeper insight to adiabatic and non-adiabatic electron transfer and nuclear tunneling in ET and PCET. Crucially, the developed rate theories can be seamlessly combined with modern computational methods based on (GCE-)DFT to facilitate self-consistent evaluation of rate constants without experimental parameters. The fixed potential rate theory will expand the type of systems, conditions, and phenomena in electrocatalysis amenable for first principles modelling.

The paper is organized as follows. In Section 2 a general rate theory and TST within GCE are developed. Rest of the paper focuses on ET and PCET kinetics within GCE. Section 3 shows how the adiabatic barrier and rate of ET and PCET reactions are computed using GCE-EVB and free energy perturbation theory to developed a fixed potential version of Marcus theory. Tafel slopes and other useful quantities as extracted from GCE-EVB are analyzed. In section 4 prefactors and non-adiabatic rate constants are derived for ET and PCET reactions with generalized first-principles Hamiltonians and many-electron wave functions. A simple computational demonstration of the GCE-EVB for Au-catalyzed Volmer reaction is presented in Section 5. Next, additional computational aspects for evaluating the rate constants are discussed in 6. Finally, the advances and results are summarized.

2. Rate theory in the grand canonical ensemble

2.1. Ensemble considerations

Discussion in the introduction highlights that the electrode potential affects both the reaction barrier and the prefactor in complex ways. Thus, the potential should be treated explicitly rather than as a simple corrective parameter as often done in theoretical and computational models used in electrocatalysis. We have recently shown that both electrochemical thermodynamic quantities for both classical and quantum particles can obtained rigorously from GCE multi-component DFT[3]. In the present context, the key realization is that GCE provides a rigorous and natural way to compute all thermodynamic expectation values at fixed electrode potentials by including the electrode potential explicitly in the \textit{ab initio} Hamiltonian (see Supporting Information in [3]). As shown below, fixed potential rate constants are GCE expectation values of...
canonical rate constants and extending canonical rate theory provides a powerful and
general machinery for computing electrochemical rate constants.

To extend (micro)canonical rate theory to the GCE, only particle conserving
reactions are considered. Thus, only a state with \(N\) particles can be converted to state
with \(N\) particles but the population and probability of \(N\) particle states is determined by
the GCE density operator. As a result, all equilibrium quantities are always well-defined
but jumps between states with unequal number of particles are suppressed. In general
this is not expected to limit the applicability of the rate expressions derived in this work;
if a quantum system is characterized by particle conserving operators (\(\hat{H}\) Hamiltonian,
\(\hat{S}\) entropy, and \(\hat{N}\) particle number), even time-dependent observables are obtained as
ensemble weighted \((p_n)\) expectation values from
\[
O(t) = \text{Tr}\left[\hat{\rho}\hat{U}(t_0, t)\hat{O}(t)\hat{U}(t, t_0)\right] = \sum_n p_n \langle \psi_n | \hat{U}(t_0, t)\hat{O}(t)\hat{U}(t, t_0) | \psi_n \rangle
\]
which do not include changes between states with
different number of particles when both the propagator \(\hat{U}\) and the operator \(\hat{O}\) are
particle conserving.[76] Hence, even explicit propagation of the wave function does not
allow sudden jumps in particle numbers or jumps between states with different number
of particles.

In a similar way, particle fluxes needed for the general flux formulation of rate
theory (see below) can be applied within the GCE as long as (local) equilibrium is
maintained.[77] This implies that the Hamiltonian is time-independent and that only
particle conserving reactions contribute to the rate constant according to the grand
canonical distribution[77]. Yet the computation of correlation functions and fluxes
poses both theoretical and computational difficulties. While both may in principle
be directly computed within GCE[77], the computation includes the coupling of the
system to the particle reservoir and introduces the reservoir time scales. Furthermore,
rate calculations require extensive sampling of reactive trajectories for which the particle
number is equal at times \(t\) and \(t + \tau\). This is because the GCE phase space volume is
not globally conserved and Liouville theorem does not hold in general. As a result, the
computed ensemble properties will depend on time if the system is not in equilibrium
or is non-stationary \(i.e\). when the phase space distribution function \(\rho(q,p,N,t)\) is not
stationary[77, 78, 79] ( \(dt\rho(q,p,N,t) \neq 0\) and \(p\) and \(q\) are momentum and position,
respectively).

In the context of the present work it is important to notice that both equilibrium
\((dt\rho(q,p,N,t) = 0\) at \(t \to \infty\)) and instantaneous \((\lim_{t \to 0^+})\) properties are uniquely
defined in the GCE[77, 79]; both qualities are absolutely essential in order to formulate
the rate and transition state theories within GCE.

Based on the above discussion, only equilibrium and instantaneous quantities are
used for formulation the GCE rate theory below - otherwise running GCE-dynamics or
making assumptions on the reservoir-system couplings need to be enforced. Hence, non-
equilibrium processes cannot be treated using the approaches presented in this paper.

Another limitation of the current approach is that electron transfer kinetics from
the electron "bath" to system (see Figure 1) are assumed fast, a condition satisfied
Grand canonical rate theory

by well-conducting electrodes. Neither of these limitations are should greatly limit the applicability of the approach for electrocatalytic or electrochemical reactions. In these reactions the electron bath is provided by a conducting electrode and equilibrium conditions are controlled by constant temperature and potential which also provide the natural control parameters in the GCE utilized in this work.

It is noted that mass transfer in electrochemical systems is not in equilibrium or even steady-state. However, the reaction rate coefficients are independent of particle fluxes and concentrations and therefore the elementary rate constants can be characterized by their equilibrium values as long as the Hamiltonian of the quantum part is time-independent and particle conserving.

2.2. General grand canonical rate theory

After establishing the particle conserving and equilibrium nature of the rate constants, the GCE rate constants can be formulated. To allow various types of reactions to be described, the canonical rate expression due to Miller[70, 71, 72, 80] is adopted:

\[ k(T, V, N)Q_I = \int dEP(E) \exp[-\beta E] = \lim_{t \to \infty} C_{fs}(t) \]  

(1)

where \( Q_I \) is the canonical partition function of the initial state, and \( \beta = (k_B T)^{-1} \).

The first expression is written in terms of transition probability at a given energy \( P(E) \). The second expression utilizes a canonical flux-side correlation function \( C_{fs}(t) = \frac{1}{(2\pi \hbar)^{f}} \int d\mathbf{p} d\mathbf{q} \exp(-\beta H) \delta[f(\mathbf{q})] \dot{\mathbf{q}} h[f(\mathbf{q}_t)] \) for \( f \) degrees of freedom. \( \delta[f(\mathbf{q})] \) constrains the trajectories to start from the dividing surface, \( \dot{\mathbf{q}} \) is the initial flux along the reaction coordinate, and \( h[f(\mathbf{q}_t)] \) is the side function which includes the dynamic information whether a trajectory is reactive or not.

Based on the discussion above, only the \( t \to 0^+ \) and \( t \to \infty \) should be considered for the flux-side correlation function in the equilibrium rate expressions. The rate from either the transition probability and flux-side formulations are equivalent. Depending on the choice of \( P(E) \) or \( H \) and \( h[f] \) non-adiabatic and adiabatic (nuclear) quantum effects are included in the rate.[81, 82, 83, 84]

It is noteworthy that \( P(E) \) and \( C_{fs} \) are computed using only particle conserving operators.[71] Therefore, the conditions discussed above are satisfied when (1) is used as the starting point for formulating the rate constants within GCE. To compute reaction rates at fixed potentials a straight-forward, yet novel, extension of the canonical rate theory to the GCE is made:

\[ k(\mu, V, T)\Xi_I = \frac{1}{2\pi} \sum_{N=0}^{\infty} \exp[\beta \mu N] \int_{-\infty}^{\infty} dE \exp[-\beta E_N] P(E_N) \]

\[ = \sum_{N=0}^{\infty} \exp[\beta \mu N] k(T, V, N)Q_0 = \lim_{t \to \infty} C_{fs}^{\mu}(t) \]  

(2)
where $\Xi_I = \exp[\beta \mu N]Q_I$ is the initial state grand partition function and $k(T, V, N)$ was introduced in (1). Above, $N$ is the number of species (nuclear or electronic) in the system and $C_{fs}$ is the GCE flux-side function. The previous equation shows that all canonical rate equations can be applied to electrochemistry within GCE approach and that fixed potential electrochemical rate constants are GCE averaged canonical rates constants.

The above equations are completely general and various flavors of rate theories can be extracted by invoking different Hamiltonians and transition probabilities, but they are somewhat cumbersome for computational purposes. Indeed, it would be convenient if the GCE rates could be directly evaluated without explicitly summing over different particle numbers. One way to achieve this is to make the transition state theory (TST) assumption[72, 71, 70] but generalized to GCE herein. In canonical TST, the instantaneous limit $t \to 0_+$ $C_{fs}(t)$ is considered corresponding to the assumption that there are no recrossings of the dividing surface. Both quantum/classical and adiabatic/non-adiabatic TSTs are written as [85, 86, 87, 88]

$$k_{TST}(T, V, N)Q_I(T, V, N) = \lim_{t \to 0_+} C_{fs}(t)$$

(3)

and the exact rate is recovered by introducing a correction

$$k(T, V, N) = \lim_{t \to \infty} \kappa(t)k_{TST}(T, V, N)$$

(4)

with

$$\kappa(t) = \frac{C_{fs}(t)}{C_{fs}(t \to 0_+)}$$

where $\kappa(t)$ is the time-dependent transmission coefficient which at long times it can also be written as $\kappa = k(T, V, N)/k_{TST}(T, V, N)$.[89] Inserting this equation in (2) results in the most general grand canonical rate constant. Significantly simplified rate constants are obtained when focusing on classical nuclei and using TST. As derived in the SI section 3, for classical nuclei the TST results is [71, 72]:

$$k(T, V, \mu)\Xi_I = \sum_{N=0}^{\infty} \exp[\beta \mu N] \int dE P_{cl}(E) \exp[-\beta E]$$

$$\approx \sum_{N} \exp[\beta \mu N] \frac{k_B T}{\hbar} Q \equiv \frac{k_B T}{\hbar} \Xi \tag{5}$$

Above, $P_{cl}(E)$ denotes transition probability for classical nuclei but the electrons are of course quantum mechanical[75, 90] with details given in [72] and the SI Section 3. The previous equation shows that the structure of GCE-TST and canonical TST are similar. This is true for open system in general if memory effects are neglected[91]. To obtain the GCE rate constant without invoking the TST approximation, one can use the transmission coefficient $\kappa$ to write
Grand canonical rate theory

\[ k(T, V, \mu) = \frac{\sum_{N=0}^{\infty} \exp[\beta \mu N] \kappa(T, V, N) \frac{k_B T}{h} Q^\dagger}{\Xi_I} \]

\approx \langle \kappa \mu \rangle \frac{k_B T}{h} \Xi_I = \langle \kappa \mu \rangle \frac{k_B T}{h} \exp[-\beta \Delta \Omega^\dagger] \tag{6} \]

where it is assumed that an effective transition probability \( \langle \kappa \mu \rangle \) can be used (for additional discussion see Sections 4.3 and 6). To complete the derivation for the classical GCE rate constant, the rate is expressed in terms of grand energies with the definition \( \Omega_i = -\ln(\Xi_i)/\beta \) and \( \Delta \Omega^\dagger = \Omega^\dagger - \Omega_I \) for the GCE barrier. Above the only new assumption besides grand canonical equilibrium distribution and TST, is that the flux out of the transition state \( \langle \kappa \mu \rangle \) can be treated as an expectation value and separated from the barrier. For large enough systems and small variations in the particle number this is a justified assumption.

The above development establishes the general fixed chemical potential rate theory. Within TST approximation the rate constant is determined by the grand free energy barrier and effective prefactor. The transmission coefficient needs to be approximated but this depends on the case at hand and examples for the adiabatic and non-adiabatic harmonic GCE-TSTs expression valid for fully open system are derived in Supporting Information section 3. Theory for addressing non-adiabaticity and tunneling is presented in Section 4 and computational results will be presented separately[92].

2.3. Semi-grand canonical ensemble

The above development is valid when both nuclear and electronic subsystems are open. A significant simplification results if one assumes that the reaction rate does not explicitly depend on the number of some nuclei in the system. In a typical first principles calculation this simplification is exploited if one assumes that the system can be divided to two subsystem: 1) classical electrolyte species consisting of nuclei and electrons and 2) electrode + reactants treated either classically or quantum mechanically. Typically the number of nuclei constituting the electrode and reactant are fixed while the electrolyte and electron chemical potential are fixed. The electrolyte charge density also adjusts to maintain charge neutrality in the system.

Fixing only the electron and electrolyte chemical potentials defines a semi-grand canonical ensemble used for deriving the thermodynamics of electrocatalytic systems within GCE-DFT[3]. In the semi-grand canonical ensemble, the electrode+reactants set the external potential at a fixed electrode potential while the electrolyte adapts to changes in the electrode potential and structure and maintains charge neutrality; the electrolyte is at a fixed chemical potential but the energetics do not explicitly depend on the number of electrolyte species. In this semi-grand ensemble, summation over the number of electrode/reactant nuclei or the electrolyte species is not needed. This scheme
is employed in first principles modelling within GCE and Poisson-Boltzmann models[3], for example.

Herein the semi-GCE is applied to derive rate constants as a function of the electrode potential. From now on, I assume that the reaction rates depend explicitly only on the number and/or chemical potential of electrons in the system. Then, the state of the system is determined by $T$, $V$, number of nuclei of the electrode+reactant $N_N$, chemical potential of the electrolyte, chemical potential of the electrons $\mu_n$, and number of electrons in the system $N$ unless explicitly specified otherwise. Electroneutrality is maintained by the electrolyte. A widely utilized harmonic TST rate for constant number of nuclei and constant electrochemical potentials are derived in section 3 of the Supporting Information.

3. Adiabatic barriers and rates from GC-EVB

To compute the GCE-TST rate at a given electrode potential, the grand energy barrier in (6) needs to be obtained. For electronically adiabatic reactions methods like the constant-potential[20] nudged elastic band[93] can be used. However, one is usually interested in rates as a function of the electrode potential and, hence, the barrier needs to be obtained for a range of electrode potentials which is computationally expensive.

As shown below, an alternative method for computing the grand energy barrier is to formulate a Marcus-like[62] approach within GCE. Marcus theory can be viewed as special case of the empirical valence bond (EVB) theory[94] commonly utilized in electron[62] and proton transfer theories.[65, 94, 95, 96, 97] Here, I present a novel extension of the canonical thermodynamic perturbation theory to the GCE to facilitate derivation of a GCE-EVB rate theory (see SI sections 4 and 5). The GCE-EVB theory developed herein provides a theoretically well-justified and computationally affordable way to obtain fixed potential barriers at various electrode potentials; the adiabatic barrier needs to be explicitly computed only at a single electrode potential while barriers at other potentials can be obtained using well-defined extrapolation of (15) making the approach particularly suitable for large scale kinetic screening studies and deriving free energy relationships from the bottom up. The utility of the GCE-EVB theory is demonstrated in Section 5.

In canonical EVB and Marcus theories the initial and final states are presented using diabatic states, effective wave functions and free energies[62]. This can be extended to GCE by using two effective, fixed potential surfaces which represent a GCE-statistical mixture of states with probabilities given by the density operator in GCE (see Section of 2 the Supporting Information and our previous work in [3]). Importantly, the diabatic states obtained using the GCE density operator naturally include many-body effects of the coupled electrode-reactant-solvent system and the complexity of the electrochemical interface is explicitly included in the model. Also, there is no need to decompose the rate constants to orbital dependent quantities and the electrode are fully (see Section 1 in the Supporting Information for additional discussion). Then, two grand canonical diabatic
all-electron wave functions are used to form an effective diabatic GCE Hamiltonian. This is analogous to molecular Marcus theory utilizing a canonical diabatic Hamiltonian containing an initial (oxidized) $I$ and final (reduced) molecule $F$.

Following the treatment in the Supporting Information Section 4, an effective $2 \times 2$ grand canonical Hamiltonian in (7) can be formed. The resulting form is analogous to the canonical EVB methods[94], electron[62], proton[96, 97] and proton-coupled electron[65] theories. The present form is, however, crucially different from its predecessors; based on the approach developed in this work, all quantities are defined and computed at fixed electrode potentials. In the basis two GCE diabatic states the effective Hamiltonian is

$$H_{GCE-dia} = \begin{bmatrix} \Omega_{II} & \Omega_{IF} \\ \Omega_{FI} & \Omega_{FF} \end{bmatrix}$$

as derived in Supporting Information Section 4. Here the diagonal elements are the grand energies of the initial (II) and final (FF) systems. The off-diagonal elements account for the interaction and mixing between the initial and final states. When this $2 \times 2$ diabatic Hamiltonian is diagonalized, the ground and excited adiabatic states are obtained. In this way the off-diagonal elements can be fitted so that diagonalization of (7) produces the adiabatic grand canonical potential energy surface obtained separately from e.g. a NEB calculation.

Finally, note that the (diabatic) grand canonical states correspond to a single electron density which is guaranteed by the Hohenberg-Kohn-Mermin[4, 3] to be unique for a given electrode potential. If a general quantum mechanical Hamiltonian is used, bond breaking is naturally included in the GCE-EVB model. The only disambiguity is the definition of diabatic states. In principle it is also possible to add other, possibly excited states as basis states. In practice the GCE diabatic energies, $(\Omega_{II}$ and $\Omega_{FF})$, can be computed directly by applying using e.g. cDFT[98, 99, 100] with fixed potential DFT as discussed in Section 6 and shown in Section 5.

### 3.1. Computation of diabatic GCE energy surfaces and barriers

Here it is shown how the GCE-EVB parameters can be obtained from atomistic simulations. An approach often used in molecular simulations for constructing the diabatic free energy curves is to sample the diabatic potentials along a suitable reaction coordinate. For canonical ET, PT, and PCET reactions the reaction coordinate is the energy gap between the two diabatic states as shown by Zusman[101] and Warshel[102]: $\Delta E_{gap}(R) = E_F(R) - E_I(R)$. From the sampled energy gap, free energy curves are obtained as $A(R) = -k_B T \ln(p(E_{gap}(R))) + c$. If the distribution is Gaussian ($p(E_{gap}(R)) = c \exp[-(\Delta E_{gap} - \langle \Delta E_{gap} \rangle)^2/2\sigma^2]$), the resulting free energy curves a parabolic. The diabatic barrier in EVB or Marcus theory is then obtained from the intersection of the initial and final diabatic curves[103, 104, 105, 106].

Within GCE, the energy gap is simply $E_{gap}(R; \mu) = \sum_{N,i} p_{N,i} E_{gap}(R_i, N)$. As shown in the SI section 5, the gap distributions can be formulated and computed by
generalizing Zwanzig’s[107] canonical free energy perturbation theory to the GCE. This route provides a rigorous way to derive the reaction barrier for in terms of diabatic states and energies as presented in the Supporting Information Section 5. The reaction energy barrier can be computed from the initial-final state energy gap distribution functions using a well-known formula[102, 108, 109, 110, 111, 112, 113]

$$k_{IF} = \kappa \frac{\exp[-\beta g_I(\Delta E^\dagger)]}{\int d\Delta E \exp[-\beta g_I(\Delta E)]} = \kappa p_I(\Delta E^\dagger)$$ (8)

where $g_i(\Delta E)$ is the free energy curve in state $i$ as a function of the energy gap, $p_I(\Delta E^\dagger)$ is the gap distribution at the transitions state, and $\kappa$ denotes an effective prefactor. The reaction rate is determined by the energy gap distribution function $p_I(\Delta E) = \langle \delta(\Delta E(R) - \Delta E) \rangle_I$ from equation (S30) of the Supporting information.

While the approach is general and valid for complex reaction, assuming that $E_{\text{gap}}(R; \mu)$ is Gaussian leads to closed form equation. In this case the GCE-diabatic states are parabolic and the Marcus barrier in GCE is given by (11). As shown in the Sections 5 of the SI, the (Gaussian) gap distribution may be derived using a second order cumulant expansion resulting in

$$p_I(\Delta E) = \frac{1}{\sqrt{2\pi}\sigma_I} \exp\left[\frac{-(\Delta E - \langle \Delta E \rangle_I)^2}{2\sigma_I^2}\right]$$ (9)

where $\langle \Delta E \rangle_I$ is the energy gap expectation value in the initial state obtained from equation (S31) in the Supporting Information and $\sigma_I = \langle (\Delta E)^2 \rangle_I - \langle (\Delta E) \rangle_I^2$ is the gap variance. The Marcus relation is then obtain after standard manipulations[103, 109] yielding

$$p_I(\Delta E^\dagger) = \frac{1}{\sqrt{4k_B T \Lambda}} \exp\left[\frac{-\beta(\Delta \Omega_{FI} + \Lambda)^2}{4\Lambda}\right]$$ (10)

where $\sigma_I^2 = \sigma_F^2 = 2k_B T \Lambda = k_B T \langle (\Delta E)^2 \rangle_I - \langle (\Delta E) \rangle_I^2$, $\Lambda$ is the fixed potential reorganization energy and and $\Delta \Omega = (\langle \Delta E \rangle_I + \langle \Delta E \rangle_F)/2$ is the reaction grand energy as depicted in Figure 2. Finally, the Marcus-like expression within GCE is

$$k = \frac{\kappa}{\sqrt{4k_B T \Lambda}} \exp\left[\frac{-\beta(\Delta \Omega + \Lambda)^2}{4\Lambda}\right]$$ (11)

The energy barrier of (11) is the diabatic energy barrier. The adiabatic barrier is estimated from (7) using the methods discussed in Section 3.2 below. One caveat to keep in mind is the more involved computation of $\kappa$ within the GCE as shown in Section 4. The above result may safely be used when $\kappa \approx 1$ for all particle numbers meaning that the reaction is always fully adiabatic and classical. An extension to non-adiabatic reactions is discussed in Section 4.3.
3.2. Implications of the canonical GCE-EVB rate theory

If the diabatic grand energy surfaces are symmetric and quadratic they have the same curvature and reorganization energy. In this case, the diabatic grand energy barrier is estimated from (11). The assumption on equal curvature can be relaxed by specifying an asymmetry parameter $\alpha_{as}$ as

$$\alpha_{as} = \frac{\Lambda_I - \Lambda_F}{\Lambda_I + \Lambda_F}$$

in terms of the reorganization energies for both the initial and final states $\Lambda_I$ and $\Lambda_F$, respectively. The transition state is located at the crossing point

$$x^\dagger/\xi = -\frac{1}{\alpha_{as}} + \frac{1}{\alpha_{as}} \sqrt{1 - \alpha_{as} \left( \alpha_{as} - \frac{4\Delta\Omega}{\Lambda_I + \Lambda_F} \right)}$$

(13)

With these definitions the asymmetric diabatic Marcus barrier and rate become

$$\Delta\Omega^\dagger = \frac{1}{4} \Lambda_I \left( x^\dagger/\xi - 1 \right)^2$$

(14a)

$$k \approx \frac{\kappa}{\sqrt{4k_B T \Lambda_I}} \frac{1 + \alpha_{as}}{1 + \alpha_{as} x^\dagger/\xi} \exp \left[ -\beta \Delta\Omega^\dagger \right]$$

(14b)

When $\alpha_{as} \to 0$, the regular Marcus barrier and crossing point are obtained. In Figure 3 the effect of asymmetry and reaction energy to the reaction barrier and location of the transition state are compared. It can be seen that both the barrier heights and its location are affected by the asymmetry and reaction energy.

While the Marcus-like equation results in a diabatic barrier, the adiabatic reaction barrier can be extracted from the diabatic barrier by diagonalizing (7). The adiabatic
Figure 3. Left: EVB curves at different different asymmetries $\alpha_{as}$. The final state reorganization energy is $\Lambda_F = 40$ while the initial state reorganization energy $\Lambda_I \in [10, 80]$. The reaction energy is $\Delta\Omega = 0$ for all curves. Right: EVB curves as a function of the reaction energy: $\Delta\Omega \in [-15, 15]$ and $\Lambda_F = 40$. The blue (red) curve corresponds to $\Lambda_I = 40$ ($\Lambda_I = 60$). Both: The dashed line at $x = 0$ indicates the position of the transition state when $\Lambda_I = \Lambda_F$ and $\Delta\Omega = 0$. The curve crossing point equals $\Delta\Omega^{\dagger}_{dia}$

barrier can also be obtained from (11) using the Hwang-Åqvist-Warshel adiabaticity correction[115, 116]

$$\Delta\Omega_{ad,EVB}^{\dagger} = \frac{(\Delta\Omega + \Lambda)^2}{4\Lambda} - \Omega_{IF}(x^\dagger) + \frac{(\Omega_{IF}(x^\dagger))^2}{\Delta\Omega + \Lambda}$$

(15)

where $\Omega_{IF}$ is the off-diagonal matrix of the GCE-EVB Hamiltonian in (7). If the Condon approximation is used, the above equation is greatly simplified as $\Omega_{IF} \approx \Omega_{IF}(x^\dagger) \approx \Omega_{IF}(x^\dagger)$ becomes a geometry-independent constant.

Next changes in the adiabatic GCE-EVB barrier as function of the parameters is analyzed. From the schematics shown in Figures 2 and 3, one can observe that changes of the minima along the reaction coordinate correspond to horizontal displacements of the diabatic states and changes in $\Lambda$. Vertical changes correspond to changes in the reaction grand energy $\Delta\Omega$. In the canonical ensemble the barrier is taken to vary only as a function of the reaction energy which is valid when the reorganization is independent of electrode potentials. This is expected to be the case for outer-sphere, electronically non-adiabatic reactions (this assumption is made in Section 4). However, reorganization energy of inner-sphere reactions taking place on or near the electrode surface may depend
on the electrode potential. For instance, it is known that water structure near electrode surfaces is sensitive to both electrode materials, pH, and electrode potential, among other factors.[117]. Therefore, the reorganization energy should not be considered as a simple constant and investigations along this direction are on their way.

Focusing on the reaction grand energy, it is easy show that under equilibrium conditions, $\Delta \Omega = 0$ and the corresponding reorganization energy $\Lambda^0$, the adiabatic barrier is

$$\Delta \Omega_{ad,EVB}^{0,4} = \Lambda^0 - \Omega_{IF} + \frac{(\Omega_{IF})^2}{\Lambda} \approx \frac{\Lambda^0}{4} - \Omega_{IF}$$  \hspace{1cm} (16)

which leads to $\Lambda^0 = 4(\Delta \Omega_{ad,EVB}^{0,4} + \Omega_{IF}) \approx 4\Delta \Omega_{dia}^{0,4}$ assuming that $\Omega_{IF} \ll \Lambda^0$. At the equilibrium point, the overpotential is, $\eta = \Delta \Omega = 0$. Assuming for a moment that $\Lambda \approx \Lambda^0$ and replacing the solution for $\Lambda^0$ in (15) gives the diabatic barrier as

$$\Delta \Omega_{dia}^{0,4} = \Delta \Omega_{dia}^{0,4} \left(1 + \frac{\Delta \Omega}{4\Delta \Omega_{dia}^{0,4}}\right)^2 = \Delta \Omega_{dia}^{0} + \frac{\Delta \Omega}{2} + \frac{(\Delta \Omega)^2}{16\Delta \Omega_{dia}^{0,4}}$$  \hspace{1cm} (17)

Inserting (17) in (15) results in the adiabatic reaction barrier as

$$\Delta \Omega_{ad,EVB}^{0,4} = \Delta \Omega_{ad,EVB}^{0,4} + \Delta \Omega + \frac{(\Delta \Omega)^2}{16\Delta \Omega_{dia}^{0,4}}$$  \hspace{1cm} (18)

This result is well-known in the canonical EVB and Marcus theories. Note however, that in the GCE this is valid only for constant reorganization energies or small changes in the electrode potential. Under the constant reorganization energy assumption, (18) shows that small changes in the electrode potential and hence the driving force $\Delta \Omega$, result in a linear dependence between the barrier and reaction energy. However, at larger driving forces, a non-linear dependence appears and which is further complicated by the potential-dependent reorganization energy.

In general, the overpotential can be manipulated easily by changing the electrode potential which is in turn directly related to the absolute electron electrochemical potential as $E^{M}(abs) \sim -\tilde{\mu}_n$.\[3, 118, 119\] It is important to notice that for microscopic systems usually considered within GCE-DFT keeping $\tilde{\mu}_n$ fixed leads to changes in the number of electrons between the initial and final states. In this respect, it is interesting to study and understand how the reaction kinetics depend on the electrode potential in the GCE picture. An experimentally meaningful approach is to study $-\partial r(T,V,\tilde{\mu}_n)/\partial \tilde{\mu}_n$ as done in a Tafel analysis, for example. Tafel analysis can also be understood in a more general context of Brønsted-Evans-Polanyi (BEP) and other (linear free) energy relations measuring the change of reaction rate when the reaction energy is changed.\[120, 121, 122\] In fact both Tafel and BEP analyses measure the reaction rate as a function the reaction driving force. For macroscopic electrochemical reactions the driving force is measured in terms of the over-potential while in microscopic calculations the driving force is the free energy. These two quantities are linked by $|\Delta \eta| = |\Delta \tilde{\mu}_n| = |\partial \Delta \Omega / \partial n|$. In the GCE approach, both the BEP and Tafel coefficients maybe computed from a single
expression. Defining the rate constant as a function of the electrode potential $E$ as $k(E) = k(E = 0)A(E)\exp(-\beta\alpha E)$ in terms of the prefactor $A$ and the Tafel-BEP coefficient $\alpha$. From this, the Tafel-BEP coefficient is obtained using [2, 120, 121]

$$\frac{d\ln k(E)}{dE} \approx -\beta\alpha \rightarrow \alpha = -\beta^{-1}\frac{d\ln k(E)}{dE} \quad (19)$$

where constant $\alpha$ and prefactor are assumed. Within GCE-EVB $\alpha$ is obtained in terms of the reorganization and reaction energies

$$-\beta\alpha = \frac{d\ln k(\Delta\Omega, \Lambda)}{dE} = \frac{\partial \ln k}{\partial \Delta\Omega} \frac{\partial \Delta\Omega}{\partial E} + \frac{\partial \ln k}{\partial \Lambda} \frac{\partial \Lambda}{\partial E} = \frac{\partial \ln k}{\partial \Delta\Omega} \frac{\partial \Delta\Omega}{\partial \mu_n} \frac{\partial \mu_n}{\partial E} - \frac{\partial \ln k}{\partial \Lambda} \frac{\partial \Lambda}{\partial \mu_n} \frac{\partial \mu_n}{\partial E} = -\gamma\Delta\Omega' - c\Delta\Lambda' \quad (20)$$

where the first term measures how the rate changes as a function of the reaction energy, $\gamma$ denotes a BEP coefficient and $\Delta\Omega'$ denotes the grand energy change as a function of the over-potential. The second contribution is unique to the GCE formulation and appears novel. This contribution measures the sensitivity of the rate to changes in the reorganization energies. In other words, this contribution measures how the initial and final states are displaced by changes in the electrode potential. This unconventional contribution can be observed in e.g. the Volmer reaction treated in [67] with a model Hamiltonian and will be discussed in more detail in a future publication[92].

Let us focus first on the $\Delta\Omega'$ term. To facilitate this analysis, one recognizes that $\Delta\Omega = (A_F(\langle N_F \rangle) - A_I(\langle N_I \rangle) - \mu_n(\langle N_F \rangle - \langle N_I \rangle))$. For macroscopic systems, chemical reactions have $N_F = N_I$ while simple electrochemical steps have $N_F = N_I \pm 1$. Then for chemical reactions $\Delta\Omega = \Delta A$ and the variation $\Delta\Omega'$ is expected to be small. For electrochemical reactions at the macroscopic limit, a particularly straightforward estimate is obtained from the computational hydrogen electrode (CHE) concept.[123] Within the CHE approach the reaction energy $\Delta\Omega \approx \Delta A^0 \mp \eta$ for PCET steps with $\Delta A^0$ computed without any bias potential. Hence, within CHE, $\alpha_{CHE} = \gamma$ for PCET steps and zero otherwise. Similar reasoning holds also for simple (outer-sphere) ET reactions in macroscopic systems as shown in Section 6 of the SI. For these reactions $\Delta\Omega \approx \Delta A^0 \mp \text{constant} \times \eta$ and $\Delta\Omega' = \mp\text{constant}$.

For microscopic systems, however, such a simple relationship does not hold in general and models such as GCE-DFT can be used for computing $\Delta\Omega'$ explicitly. Thus far, $\Delta\Omega'$ has been reported in only few studies[20, 21, 124]. In these works and in Section 5, $\Delta\Omega$ is found to exhibit a roughly linear dependence on the applied potential. $\Delta\Omega'$ is expected to be a constant close to unity for electrochemical reactions and close to zero for chemical reactions.

Next, the BEP $\gamma$ of Eq (20) is analyzed. Using the diabatic barriers in (17) (obtained assuming constant reorganization energy and constant prefactor), one obtains
\[
\gamma = \frac{\partial \ln k(T,V,\bar{\mu}_n)}{\partial \Delta \Omega} \bigg|_{T,V} \approx \frac{\partial \ln e^{-\beta \Omega^\dagger}}{\partial \Delta \Omega} \bigg|_{T,V} = -\beta \left[ \frac{1}{2} + \frac{\Delta \Omega}{8 \Delta \Omega^\dagger_{\text{dia}}} \right] = -\beta \left[ \frac{1}{2} + \frac{\Delta \Omega}{\Lambda^0} \right] \tag{21}
\]

which results in \( \alpha = -\Delta \Omega' (1/2 + \Delta \Omega/2 \Lambda^0) \). From the above equation, it is seen that \( \gamma \) is not a simple constant but depends linearly on the reaction driving force. If the reorganization energy is small the dependence on the reaction grand energy becomes more pronounced as demonstrated for the Au-Volmer reaction in Section 5. In general, based on the generalized BEP-Tafel energy identities, the following relationships are expected:

- If the quadratic part in (17) is neglected and the reorganization energy is assumed a constant, one obtains the Butler-Volmer (BV) barrier. In this case the barrier depends linearly on the applied potential as \( \Delta \Delta \Omega^\dagger_{\text{dia,EVB}} \approx 0.5(A_F(\langle N_F \rangle) - A_I(\langle N_I \rangle) - \mu_{\text{el}}(\langle N_F \rangle - \langle N_I \rangle)). \) \( \mu_{\text{el}} \) is implicitly referenced against \( \mu_{\text{el}} = 0 \) and can be converted to the over-potential as \( \mu_{\text{el}} - \mu_{\text{el}}^{eq} = \Delta \eta \). Note that \( \Delta \Delta \Omega^\dagger_{\text{dia,EVB}} \) is not expected to be linear for finite-sized systems. Again, for macroscopic systems \( \langle N_F \rangle = \langle N_I \rangle \) and \( \Delta \Delta \Omega^\dagger_{\text{dia,EVB}} = \Delta \Delta A^\dagger_{\text{dia,EVB}} = 0.5(A_F - A_I) \) which is the BEP result. The BV relationship is obtained by treating a specific reaction type. For example, in a typical ET, PT, or PCET the potential-dependent reaction free energy is given by \( \Delta A = \Delta A(\eta = 0) \pm (n \eta) \). Using this for \( \Delta \Delta A = \pm 0.5 n \eta \).

- Non-linearity of the grand energy barrier has two contributions: non-linearity of the diabatic barrier and the potential-dependent reorganization energy. For macroscopic systems non-linearity is established by including the quadratic part of the diabatic barrier in the model. Lately\(^{29, 31, 20, 21}\) this has been observed computationally and it is pleasing that the GCE-EVB picture seems qualitatively correct.

A spectacular feature of canonical Marcus and EVB theory is the observation of an inverted region \( i.e. \) the rate constant starts to decline as the reaction becomes more exothermic. However, the inverted region has not been observed for electrochemical reactions even at large over-potentials. The grand canonical Marcus rate of (11) seems to predict an inverted region for highly exothermic conditions. However, as written in the Tafel equation (20) the rate as a function of the over-potential depends has a complicated dependence on the potential, reorganization energy, and the reaction energy. The BEP relation would indeed predict an inverted region which is suppressed if \( \Delta \Omega' \approx 0 \). Also the reorganization energy should saturate at large overpotentials. As a result, the Tafel slope would approach zero as predicted by the
Marcus-Hush-Chidsey[125], Dogonadze-Levich-Kuznetsov[49, 48], Newns-Anderson-Schmickler, Soudackov-Hammes-Schiffer[53] models of ET and PCET [63] (see also Supporting Information Section 1). At the moment, this is purely speculation as there is not enough computational nor theoretical evidence on the behaviour elementary rate constants as a function of the electrode potential. Furthermore, for very small barriers, reorganizational dynamics of the surroundings may start to limit the reaction and dynamical properties of the surroundings need to addressed as discussed in Section 6.

To summarize, the generalized BEP-Tafel relationships have been derived from a microscopic perspective using grand canonical rate theory. Both variation in the reaction energy barrier and the transition state location as a function of the potential can be predicted using just a few parameters. This is demonstrated for the acidic Volmer reaction in Section 5. The general form of the BEP-Tafel relation is given in (20). For small over-potentials, the rate is expected to depend linearly on the applied potential. For larger over-potentials non-linear dependence is predicted, especially reactions for which the reorganization energy is small. The taken GCE perspective also predicts a novel potential-dependent reorganization energy which is supported by model Hamiltonian calculations[67] and will be addressed carefully in future publications.

4. Non-adiabatic ET and PCET reaction rates within GCE

As shown above, computation of fixed potential rates for of electronically adiabatic reactions does not yield any fundamental difficulties as compared to the canonical case; after finding the barrier, one can simply use a simple TST-like expression to compute the reaction rate using grand free energies. Besides the reaction barrier, rates depend on the prefactor which is crucial for modelling ET, PT, and PCET reactions which often feature (non-)adiabatic tunneling. Given the importance of ET, PT, and PCET in both applications and fundamental studies, the prefactors are treated here for consistency of the general framework while the computational applications will be presented separately[92].

Including the prefactor beyond TST presents some difficulties and care is needed. In particular, the treatment of non-adiabatic processes is difficult; electronic transition matrix elements are not defined for states with different number of electrons when only particle conserving operators are used. In other words, the transition needs to be particle conserving. The non-adiabatic flux-side correlation function utilizes a projection operator which is explicitly depends on the particle number.[126] Hence, developing a transition probability which is independent of the particle number is not straightforward and therefore one cannot directly use the effective GCE-EVB states developed in Section 3 to compute the electronically non-adiabatic rate. Instead, the electronic transition matrix element needs to be computed separately for each canonical transition which preserve particle number upon transition. Afterwards, a summation over the canonical rates is performed to express the non-adiabatic ET/PCET rate as a GCE
expectation value.

To obtain the non-adiabatic TST rate, the Golden-rule approach is used herein. In the canonical ensemble, the Golden-rule formulations are well established.[33, 48, 49, 104] Below the theory of non-adiabatic ET and PCET rates within GCE is developed. It is stressed that the non-adiabatic approach is inherently quantum mechanical and ET, PT, and PCET reactions describe quantum mechanical tunneling processes.

4.1. Non-adiabatic ET rate

To start with, localized electronic states \(|iN\rangle\) are specified as eigenstates corresponding to the electronic Hamiltonian \(\hat{H}_N^{\text{el}}\). Electronic states are defined for initial \((i)\) and final \((f)\) states with a fixed number of particles \((N)\). Then the electronic energies for the initial and final states at fixed particle number at nuclear geometry \(Q\) are

\[
\langle iN | \hat{H}_N^{\text{el}} | iN \rangle = \epsilon_{iN}(Q) \quad \text{and} \quad \langle fN | \hat{H}_N^{\text{el}} | fN \rangle = \epsilon_{fN}(Q)
\]  

(22)

Within the Born-Oppenheimer approximation (BOA), the nuclear wave functions and their energies \(\epsilon\) in the initial \(|mN\rangle\) and final \(|nN\rangle\) electronic states are obtained from

\[
[\hat{T}_Q + \epsilon_{iN}(Q)] |mN\rangle = \epsilon_{mN} |mN\rangle \quad \text{and} \quad [\hat{T}_Q + \epsilon_{fN}(Q)] |nN\rangle = \epsilon_{nN} |nN\rangle
\]

(23)

where \(\hat{T}_Q\) is the nuclear kinetic energy. Within BOA, the total vibronic wave function and the corresponding energy factorize as

\[
|mN\rangle = |iN\rangle |mN\rangle \quad \text{and} \quad E_{mN} = \epsilon_{iN} + \epsilon_{mN}
\]  

(24a)

\[
|nN\rangle = |fN\rangle |nN\rangle \quad \text{and} \quad E_{nN} = \epsilon_{fN} + \epsilon_{nN}
\]

(24b)

As the different energy contributions are additive, the canonical partition functions can be factorized

\[
Q_i^N = \exp[-\beta \epsilon_{iN}] \sum_m \exp[-\beta \epsilon_{mN}] \quad \text{and} \quad Q_f^N = \exp[-\beta \epsilon_{fN}] \sum_n \exp[-\beta \epsilon_{nN}]
\]

(25)

At this point all relevant canonical quantities have been defined and the focus turns to the GCE formulation of the Golden-rule rate. The GCE partition function for the initial state is

\[
\Xi_i = \sum_N \exp[\beta \mu N] Q_i^N
\]

(26)

This equation is inserted in the general GCE rate expression. For the non-adiabatic limit, the Golden rule rate expression is used. As shown in Supporting Information
Sections 1 and 3, using the Golden rule expression is consistent with the general rate theory based on the flux approach if a non-adiabatic Hamiltonian and suitable flux operator are utilized. The GCE-NATST rate constant is then

\[ k_{\text{GCE-NATST}} = \frac{2\pi}{\hbar \Xi_i} \sum_N e^{-\beta(\varepsilon_{iN} - \mu_N)} \sum_{m,n} e^{-\beta \varepsilon_{mN}} \left| \langle Nnf | \hat{V}_N | imN \rangle \right|^2 \delta(E_{imN} - E_{fnN}) \]

(27)

where \( p_{mN} \) is the population of the vibronic state \(|imN\rangle\). Next, a significant simplification is made; it is assumed that the vibrational part of the canonical partition function does not depend on the number of electrons in the system. This assumption directly implies that the reorganization energy is potential independent which should be a reasonable assumption for electronically non-adiabatic reactions. As a result

\[ Q_i^N = \exp\left[ -\beta \varepsilon_{iN} \right] \approx \exp\left[ -\beta \varepsilon_{iN} \right] \sum_m \exp\left[ -\beta \varepsilon_{mN} \right] = \exp\left[ -\beta \varepsilon_{iN} \right] Q_m \]

and the GCE partition function becomes

\[ \Xi_i \approx Q_m \sum_N \exp\left[ -\beta(\varepsilon_{iN} - \mu_N) \right] = Q_m \Xi_i \]

(28)

Inserting this approximation in the GCE-NATST rate expression gives

\[ k_{\text{GCE-NATST}} \approx \frac{2\pi}{\hbar \Xi_i} \sum_N \frac{e^{-\beta(\varepsilon_{iN} - \mu_N)}}{Q_m} \sum_{m,n} \frac{e^{-\beta \varepsilon_{mN}}}{p_{mN}} \left| \langle Nnf | \hat{V}_N | imN \rangle \right|^2 \delta(E_{imN} - E_{fnN}) \]

(29)

where \( p_{iN,el} = \exp\left[ -\beta(\varepsilon_{iN} - \mu_N) \right]/\Xi_{i,el} \) and \( p_{mN} = \exp\left[ -\beta \varepsilon_{mN} \right]/Q_m \).

This equation has the structure of the canonical Golden rule rate weighted by the GCE probability of being in the initial electronic state \( iN \). To simplify the notation, one can momentarily concentrate only on the canonical part of the above rate expression. As shown in the Supporting Information Section 7, using the Fourier transform presentation of the delta function, gives

\[ k_{\text{GCE-NATST}} \approx \sum_N \frac{V_{N,fi}^2}{2\hbar^2 p_{iN}} \int dt C(t) \]

(30)

where \( C(t) \) is an energy autocorrelation function (see Supporting Information Section 7). The autocorrelation function maybe extracted from time-dependent quantum or classical dynamics. However, to obtain a closed form for the rate equation, herein the autocorrelation function is expressed using a cumulant expansion[127]. Using
Grand canonical rate theory

the second order cumulant expansion, assuming that all solvent degrees of freedom are classical and taking the short time approximation\[128\] to the correlation function results in (see Supporting Information Section 7):

\[
k_{\text{GCE-NATST}} \approx \sum_N p_i N \frac{V_{N,ff}^2}{\hbar \sqrt{4 \pi k_B T} \lambda} \exp \left[ -\frac{(\Delta E_{fi}^N + \lambda)^2}{4k_B T \lambda} \right]
\]

The reorganization and reaction energies are defined as \( \lambda = E_{im}(Q_F) - E_{in}(Q_I) \) and \( E_{fi}^N = E_{fi}^N(Q_F) - E_{im}(Q_I) \) (see Figure 3.) While the above development rests on the assumption of constant reorganization energy, the solvent structure depends on the potential and charge state of the electrode and reorganization energies for reactions near the electrode may not be constant. To account for this, the reorganization energy can be further separated to inner and outer sphere components as discussed in Section 10 of the Supporting Information. If this separation is invoked, one can alleviate the assumption that the total reorganization is independent of the particle number and instead assume that only bulk solvent (outer sphere) reorganization is a constant while the inner-sphere reorganization energy depends on the particle number i.e. is potential-dependent.

4.2. PCET kinetics within GCE

The PCET kinetics is based on the PCET rate theory of Soudackov and Hammes-Schiffer. Within the canonical ensemble the relevant rate expressions were derived in Refs. [60, 65, 61, 53] and here this treatment is extended to the GCE yielding PCET rate constants at fixed electrode potentials. The PCET rate constant derivation follows a similar procedure as the one used above for the ET rates. In the case of PCET, an additional geometric variable \( q \) for the transferring proton is introduced. Within BOA, the total vibronic wave function is then

\[
|i u m N \rangle = |i N(q, Q) \rangle |u N(Q) \rangle |m N \rangle
\]

where it is explicitly written that the electronic wave function \( |i N \rangle \) depends explicitly on the proton \( q \) and system coordinate \( Q \) while the proton wave function \( |u N(Q) \rangle \) depends on the system coordinate \( Q \). The wave functions and corresponding energies are solved using equations similar to the ET case

\[
\langle i N \vert \hat{H}_N^e \vert i N \rangle = \epsilon_{iN}(q, Q) \quad \text{and}
\langle f N \vert \hat{H}_N^e \vert f N \rangle = \epsilon_{fN}(q, Q)
\]

\[
[\hat{T}_q + \epsilon_{iN}(q, Q)] |i u N \rangle = \epsilon_{iN}^i |i u N \rangle \quad \text{and}
[\hat{T}_q + \epsilon_{fN}(q, Q)] |f v N \rangle = \epsilon_{fN}^f |f v N \rangle
\]

\[
[\hat{T}_q + \epsilon_{iN}^i] |m N \rangle = \mathcal{E}_{mN} |m N \rangle \quad \text{and}
[\hat{T}_q + \epsilon_{iN}^f] |n N \rangle = \mathcal{E}_{nN} |n N \rangle
\]
where $\hat{T}_q$ and $\hat{T}_Q$ are the kinetic energy operators for the proton and other nuclei, respectively. Within BOA, the total energy of the at fixed $N$ is written as a simple sum of the three contributions:

$$E_{iumN} = \varepsilon_{iN} + \varepsilon_{uN} + E_{mN}$$  \hspace{1cm} (34)

and similarly for the final diabatic state. Furthermore, coupling constant is given as

$$\langle Nn | \hat{V}(R) | imN \rangle \approx \langle Nf | \hat{V}(R) | imN \rangle \langle Nn | mN \rangle$$  \hspace{1cm} (35)

The SHS treatment of PCET rates is valid for reactions ranging from vibronically non-adiabatic to vibronically adiabatic scenarios[129] and rate expressions for various well-defined limits have been achieved. The SHS PCET rate theories are derived following a path analogous to the derivation of ET rates and extension to the GCE is rather straightforward. As done by SHS, the Golden rule formulation is used. The details of this derivation are presented in the SI Section 11. The simplest GCE-PCET rate is given for the short time approximation of the energy gap correlation is valid in the high-temperature limit and static proton donor-acceptor $R$ distance as

$$k = \sum_{N,u} p_{iu} \sum_{v} \frac{|V(R)^N_{uv}|^2}{h\sqrt{4\pi k_B T \lambda_{uv}}} \exp \left[ -\frac{(\Delta E^N_{uv} + \lambda_{uv})^2}{4k_B T \lambda_{uv}} \right]$$  \hspace{1cm} (36)

where the reaction energy between vibrational states $iuN$ and $fvN$ is $E^N_{uv} = E_{fimN}(q_F, Q_F) - E_{iumN}(q_I, Q_I)$. The state-dependent reorganization energy $\lambda_{uv} = E_{ium}(q_F, Q_F) - E_{ivm}(q_I, Q_I)$ is assumed independent of the particle number. If some vibrational modes (besides the $R$ mode) are sensitive to changes in the particle number, they can be separated from the total reorganization energy by decomposing the total reorganization energy to inner- and outer-sphere components as shown in Section 10 of the Supporting Information. Depending on the form of the prefactor, both electronically and vibronically adiabatic and non-adiabatic limits of PCET can be reached within the semiclassical treatment[34, 130, 131] of the prefactor.

4.3. Hybrid GCE-NA-EVB model

Bridging the the NA and adiabatic EVB models developed above, vibronic or electronic diabatic states along the reorganization are considered as shown in Figure 4. As in the NA model, the hybrid model takes the reorganization of the unreactive nuclei $Q$ as the reorganization and reaction coordinate. However, unlike in the NA model, the hybrid GCE-NA-EVB model treats the reorganization coordinate at a fixed electrode potential, as done in the GCE-EVB model. The effective barrier is then $\propto \exp[-\beta(\Lambda + \Delta \Omega)^2/4\Lambda]$. At the crossing point of the initial and final states along $Q$ coordinate the vibronic/electronic diabatic states are brought in to resonance so
Figure 4. Schematic picture for electrochemical PCET. The pink (green) line depicts an initial (final) vibronic diabatic state as a function of the environment reaction coordinate. The insets show two types of proton curves along the proton transfer coordinate at the initial, transition and final solvent coordinates. The top (bottom) inset shows the electronically non-adiabatic (adiabatic) proton curves. The dashed solid (dashed) electronically non-adiabatic curve corresponds to electron localized at the initial (final) state. In each inset the black and orange curves correspond to two different electrode potentials or states with different number of electrons.

that nuclear/electron tunneling can take place. The contribution of tunneling between different canonical diabatic states depends on the applied potential. The GCE prefactor can be approximated as a GCE expectation value of canonical prefactors $\propto V_{\mu,if}^2 \approx \sum_N p_{iN}V_{N,if}^2 = \langle V_{N,if}^2 \rangle_\mu$. Combining the the barrier and prefactor leads to the NA-GCE-EVB rate constant

$$k_{NA-GCE-EVB} \approx \frac{\langle V_{N,if}^2 \rangle_\mu}{\sqrt{4k_BT\Lambda}} \exp\left[-\beta \frac{(\Lambda + \Delta\Omega)^2}{4\Lambda}\right]$$ (37)

Unlike the NA-TST rates in the previous section, the hybrid model makes of the GCE free energies. Also, unlike the GCE-EVB model, the hybrid includes a well-defined way to compute the prefactor as detailed in Section 3 of the SI. Using the Landau-Zener approach discussed in Section 6, the hybrid model offers a transparent way to interpolate
between adiabatic and non-adiabatic reactions in a single framework. This hybrid model also provides a tempting way to include and estimate non-adiabatic and tunneling effects in large scale DFT studies and material screening with kinetics.

4.4. Analysis of the non-adiabatic GCE rates

In this section the computation of prefactors was considered to go beyond the TST limit. In particular (non-adiabatic) tunneling in ET and PCET was treated. The main difficulty in the GCE non-adiabatic rate theory is the treatment of the electronic/vibronic coupling constant; this term is defined only for particle conserving transitions. This precludes the straightforward use of initial and final GCE diabatic states which have different number of electrons at the same geometry. The NA-GCE-EVB hybrid offers a well-defined way to approximate the non-adiabatic effects using GCE diabatic states but the prefactors still need to be computed using canonical states and GCE averaging. Only at the thermodynamic limit when the particle number fluctuation approaches zero can the GCE diabatic states be used for computing the coupling constant. However, at this limit the GCE-NATST is equal to the canonical NATST as only a single particle number state is populated i.e. \( p_i \) becomes a delta function at some particle number. At the thermodynamic limit either using fixed potential GCE states or fixed particle number canonical states will give equivalent results, as they should.

Even at the thermodynamic limit the present treatments differ from the traditional Dogonadze-Kutzetnotsov-Levich[49], Schmikler-Newns-Anderson[63, 64, 66], and SHS approaches. A detailed discussion is given in Section 1 of the Supporting Information and here only the main differences are high-lighted. The crucial difference is that the present formulation does not rely on the separation of the total interacting wave function to non-interacting or weakly interacting fragments. Also, in the present approach, the applied electrode potential does not only affect the electrode potential is self-consistently treated to affect all electrode, reagent, and solvent species. This way the inherent complexity of the electrochemical interface is naturally included in the Hamiltonian and the wave functions in a self-consistent manner. For instance, the work terms entering Marcus[62] or other electrochemical rate theories[67, 69] do not need to be computed in the present formalism. Another crucial difference is that the charge transfer kinetics are not decomposed into single electron orbital contributions. Instead, the work herein formulates the kinetics in terms of many-body diabatic wave functions. In the canonical ensemble, such an approach has been shown[132] to provide accurate barriers, prefactors, and overall kinetics for electron transfer reaction in battery materials.

For small systems where particle number fluctuations are pronounced the summation over particle numbers need to be performed. While straightforward in principle, the amount of calculations can seem daunting at first. However, as the populations depend exponentially on the energy and target chemical potential, \( p_{iN} \sim \exp[-\beta(E_{iN} - \mu N)] \), only a limited number of states will contribute to the summation.
In Section 8 of the Supporting Information, it is shown that for graphene, the electrode potential around the PZC ± 0.5V is accurately captured with seven different charge states. It is expected that the infinite summation can be safely reduced to summation over a small number (5–10) of different charge states covering the electrode potential range of interest. Again, at the thermodynamic limit only a single calculation per potential is needed.

5. Computational example for the Au-catalyzed Volmer reaction

Here the first demonstration of the GCE rate theory is provided. I consider the acidic Volmer reaction i.e. proton discharge which is arguably the simplest and yet relevant electrocatalytic reaction for hydrogen production and other electrocatalytic reactions. Similarly, gold can be considered as the simplest electrode material. Yet, the Volmer reaction, even on gold, is not fully understood[133] and the reaction is considered to exhibit nuclear quantum effects and even vibronic non-adiabaticity.[34, 35] As a first application of the theory and methodology derived and developed in this work, I consider an adiabatic and classical model for the acidic Volmer reaction – quantum effects and a non-adiabaticity is studied separately in a forthcoming publication[92]. The results are discussed in the GCE-EVB framework of Section 3.

The Volmer reaction is modelled as a single hydronium ion on 3x3x5 Au(111) surface as shown in Figure 5. The needed energies were computed within GCE-DFT as implemented in GPAW[134] using the surface-jellium approach[20] with a continuum solvent model for water[135]. This approach gives all the thermodynamic quantities at a fixed electrode potential. The potential-dependent minimum energy pathways are computed using a nine image nudged elastic band[93] (NEB) discretization. Geometries and NEB pathways were considered converged when the maximum force was below 0.05 eV. Constant-potential diabatic states and reorganization energies were computed using constrained DFT (cDFT) as implemented in GPAW[136]. The diabatic states are chosen as +1 state for the hydronium ($H_3O^+$) and neutral for the final water and adsorbed hydrogen ($H_2O + H^*$). A more detailed account of the computational approaches will be provided separately[92].

The reorganization energies at the equilibrium potential are $\Lambda_F = 2.1$ eV, $\Lambda_I = 3.2$ eV, and their average $\Lambda = 2.65$ eV. These cDFT computed reorganization values are in good agreement with the values used model Hamiltonian parametrizations of Huang[68] and Santos[66] but much larger than the one used by Lam[67]. The reaction asymmetry from (12) is 0.2 meaning that the transition state geometry along the reorganization coordinate is closer to the initial state. Analysis of the TST geometries at different potentials shows that that reorganization energy is best presented either by the Au-O distance or the dihedral angle between the $H_2O$ and surface.

In Figure 5 the reaction barrier is plotted as a function of the reaction energy corresponding to different electrode potentials. First, one observes that the barriers are very small for all considered electrode potentials. This is line with explicit water
Figure 5. Above: The reaction pathways at different potentials. The stars show the DFT-NEB computed TST geometry along reorganization coordinate. The stars correspond to TST geometries predicted using equation (14a). Below: The fixed potential Au(111) Volmer barrier as a function of the reaction energy. NEB[*] refers to NEB calculations of the present paper with an implicit solvent while NEB[20] are from [20] with explicit, ice-like solvent. Also the barrier and reorganization energy used in the model Hamiltonian work of [67] are shown and extrapolated using (18).

DFT results[20] at all electrode potentials and reaction energies. The figure also shows the TST location as a function of the reaction energy from both NEB-DFT and extrapolation using (14a). The extrapolation reproduces the TST geometries very well, and captures the trends in the TST location. For comparison, explicit solvent calculations exhibit a similar trend in the TST position as a function of the potential[20] as the one found here using an implicit solvent. This example demonstrates the Au-O distance is good reorganization coordinate and that the TST location is effectively captured by (14a). Unlike DFT-NEB calculations, the GCE-EVB requires just one NEB and two reorganization energy calculations to capture the TST geometry for a range of reaction energies and electrode potentials.

The results in Figure 5 also highlight that the (18) with a cDFT computed reaorganization energy provides a very accurate way for computing the adiabatic
potential-dependent energy barrier. It is also observed that the estimate for the reorganization energy used in the model Hamiltonian work of [67] is very small (∼0.3 eV) and cannot be used for predicting barriers using GCE-EVB.

Besides enabling a reliable prediction of reaction barriers and TST geometries, the results demonstrate the first GCE-cDFT calculations. Besides showing that GCE-cDFT is technically possible, the results show that ab initio computed diabatic states offer new insight to electrocatalytic reactions. In particular, the results provide a proof-of-principle that GCE-EVB can be used to accurately estimate barriers using just a single NEB calculations and a few cDFT calculations with an expense similar to a standard DFT calculation.

6. Discussion

The distinct advantage of the formalism and theory developed in this paper is that all rate equations can be readily evaluated with GCE-DFT or other first principles approaches. The presented formalism enables the treatment electrochemical and electrocatalytic thermodynamics and kinetics in terms of the prefactor and barriers in the same framework – the GCE. Therefore, the same DFT-based tools can be used to address inner-sphere and outer-sphere kinetics and thermodynamics instead of modifying or changing the theoretical and computational framework for different reaction steps[36].

By construction the rate constants include the interplay between the electronic structure, solvent, electrode potential etc. The electrode potential is self-consistently treated and all free energies and prefactors depend explicitly on the potential. This is in contrast with traditional model Hamiltonian treatments where the electrode potential rigidly shifts the Fermi-level without modifying any interactions or prefactors [64, 69] or modifies only the electrostatic interactions[34, 67]. Also, a separate computation of work terms[67, 69, 68, 137] is not needed because all relevant interaction can be directly included in the general Hamiltonian. Evaluation of chemisorption functions used for modelling interactions in the adiabatic Newns-Anderson-based models[63, 66, 67, 64, 68, 137]. Therefore, the current models are free of approximate treatment of semi-elliptic DOSs[67, 66, 137] or fitting the chemisorption functions to a computed DOS[66, 137]. For non-adiabatic models, evaluation of the coupling matrix elements does not rely on orbital-to-orbital transitions and integration over the DOS as done in traditional non-adiabatic perturbation theory -based approaches[64].

As the developed rate theory utilizes general ab initio Hamiltonians, bond formation/breaking are naturally included. This is again in contrast with model Hamiltonians which require approximate potential-independent terms to describe changes in atomic bonding [138, 139, 137]. Instead, as demonstrated herein, ET, PT, or PCET and bond rupture/formation are naturally captured with GCE-DFT. Bond formation in non-adiabatic reactions is also captured by diabatic models using DFT as demonstrated for ET[132], PCET[140] and general chemical reactions[141, 142].
As parametrization of model Hamiltonian is circumvented, adoption and evaluation of the rate expressions is straight-forward (but potentially laborious). Especially the GCE-EVB is particularly suitable for large scale computational studies of electrochemical or electrocatalytic kinetics and screening studies. One needs to evaluate the barrier at the equilibrium potential and extrapolate to other potentials using the free energy relations written in terms of the reaction (grand) free energy and solvent reorganization energy as demonstrated for the Au-Volmer reaction. The same approach also provide predictions and good estimates for Tafel slopes or BEP coefficient and the TST geometries from first principles.

While applicability and usefulness of combined DFT and GCE-EVB was demonstrated for the Volmer reaction, it is worth discussing the additional computational requirements in some detail. First, the simulation of charged systems is needed to sample the electrode potential. Electroneutrality can be enforced using some variant of the Poisson-Boltzmann models, for details see [3]. Fixed potential calculations can be accomplished within a single SCF cycle[10], or iteratively [143, 20]. Second, the solvent effects should be included in the model. For adiabatic reactions the main solvent contribution is thermodynamic and stems from (de)stabilization of different structures. For non-adiabatic reactions and GCE-EVB models rates should always be performed in the presence of a solvent; the reaction barrier is directly related to the solvent/environment reorganization energy and neglecting the solvent contributions will most likely lead to incorrect results.

Given a software capable of handling charged systems and performing constant potential calculations, adiabatic rate constants can be readily evaluated. As shown for the Volmer reaction, reaction barriers and adiabatic prefactors at constant potential are obtainable using e.g. the NEB[93] method.

Evaluation of non-adiabatic and GCE-EVB rate constants requires additional software capabilities for constructing charge/spin localized diabatic states and to evaluate the electronic coupling between these states. Also the reorganization energy, which is an excited state quantity, needs to be computed. One widely implemented and available tool for evaluating the additional parameters is the cDFT methodology[98, 99, 100] which is implemented in several DFT codes[136, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153]. The extension of cDFT to GCE was, for the first time, demonstrated and applied in this work and will be also utilized in future works. Evaluation of the vibronic/vibrational matrix elements is accomplished using e.g. a Fourier grid Hamiltonian[154] method which is easy to implement.

GCE-EVB and GCE-NA-EVB simulations should be accompanied with a constant potential simulations to compute fixed potential reaction and reorganization energies. The practicality of GCE-EVB was demonstrated for the Volmer reaction by computing all the necessary kinetic parameters using GCE-DFT and GCE -cDFT. Non-adiabatic rate constants need sampling at different charge states to evaluate the summation over the number of electrons. While this summation is in principle infinite, in practice only 5-10 charge states suffice because GCE weight is non-zero only for a few states as discussed
Grand canonical rate theory

in Section 4.4. This will also be demonstrated in forth-coming work\[92\].

A final computational aspect in applying the current approach is the interpolation between the different rate equations. Such an interpolation is needed to bridge the adiabatic and non-adiabatic rate constants because the division between inner-sphere/electrocatalytic/adiabatic and outer-sphere/non-adiabatic/electrochemical is not always straightforward. This division depends on the reaction, reaction conditions as well as \textit{e.g.} distance between the reactant and the electrode. Currently, a generally valid interpolation for fixed potentials is not available. In the canonical ensemble interpolation between electronically/vibrationally adiabatic and non-adiabatic reactions can be accomplished using the Landau-Zener formula.\[58, 103\]. In PCET, a universally valid Landau-Zener -like interpolation from a fully non-adiabatic to fully adiabatic reaction is accomplished using a semiclassical PCET prefactor.\[130\].

Besides interpolating between the adiabatic and non-adiabatic limits, the interpolation should also include the time-scale relevant solvent dynamics.\[155\] Solvent dynamics are likely to become increasingly important when the reaction is adiabatic and the reaction barrier becomes very small or vanishes. In these case the solvent reorganization will be the slowest process and the reaction prefactor should reflect this. At canonical non-adiabatic limit solvent control is usually based on the works of Zusman\[101\] or Rips and Jortner\[155\]. In the electronically adiabatic limit the solvent dynamics are often described in terms of the Kramers-Grote-Hynes theory.\[156\]. While numerous attempts have been taken\[157, 158, 159\] to obtain a universally valid interpolation between adiabatic – solvent dynamic – non-adiabatic, the author is not aware of a generally accepted construction for this interpolation. Also adapting the interpolation schemes to the fixed-potential rate theory requires care. More work is obviously needed to obtain a robust interpolation between well-defined limits in an electrochemical setting.

7. Conclusions

In this work a new theoretical formulation for computing electrochemical and electrocatalytic rate constants at a fixed potential is developed. The fixed-potential rate expressions are based on a novel formulation obtained by extending the universally valid canonical rate theory\[70, 71, 72\] to the grand canonical, fixed potential ensemble. General conditions and limitations for the fixed potential rate theory are developed. It is shown that all rate theories developed within the canonical ensemble can be transferred to the GCE. This is conceptually important because the fixed-potential rate theory enables treating all potential-driven reactions within a single formalism instead of relying on separate theories for different cases. The theoretical work presented herein provides a unified framework for computing and understanding both the barrier and prefactor for inner-sphere and outer-sphere, adiabatic and non-adiabatic, classical and quantum rates from a single formalism.

Specific rate expressions are derived for typical electrochemical ET, PT, and
PCET reactions. Fixed potential rate expression have been derived for i) general
electrocatalytic reactions with ((5)) and without ((2)) the TST approximation, ii)
electronically adiabatic ET, PT and PCET reactions using a grand canonical Marcus-
like GCE-EVB theory in (11) , and iii) tunneling and non-adiabatic contributions in
ET ((31)) and PCET ((36)) within non-adiabatic curve crossing. Also a hybrid model
bridging the EVB and non-adiabatic rate equations has been proposed. Future work
will provide interpolation between the derived adiabatic, non-adiabatic, and solvent-
controlled rate equations.

The GCE-EVB formalis enables computing the grand energy barrier in terms of
fixed potential reorganization energy and the reaction grand energy in analogy with
the canonical EVB or Marcus theory. GCE-EVB can explain and predict explain the
"Marcus-like" behavior in energy barriers and TST geometries as a function of the
thermodynamic driving force observed in recent computational work[29, 31, 20] and
herein. GCE-EVB enables also the computation of non-linear energy relationships
and Tafel slopes and general BEP-Tafel relations using just few DFT parameters;
this has shown for the Volmer reaction using fixed potential (constrained) DFT. It is
demonstrated that quantitatively accurate barriers and TST geometries can be predicted
using a few self-consistent GCE-DFT calculations. These features are expected to make
the GCE-EVB approach particularly suitable for electrocatalyst screening studies.

Besides the reaction barrier, computation of the prefactors has also been addressed.
In particular, I have focused on tunneling in electronically (and vibronically) non-
adiabatic ET and PCET reactions within the curve crossing picture. In the presented
theoretical formulation many methodological difficulties can be overcome as the
computational tools largely exist as will be demonstrated separately[92] (see also Section
6).

The developed theory can be directly combined with modern, solid-state ab initio
methods to capture the complexity of the electrochemical interface at constant potential.
In this sense, the model is fully ab initio and all parameters can be directly computed
without resorting to fitting. A set of widely implemented DFT-based tools suffices to
compute all the needed parameters in a self-consistent manner. This should enable
the computational community adopt the theoretical framework and to progress from a
thermodynamics-based description of electrocatalysis to addressing also electrocatalytic
kinetics in experimentally realistic conditions.

Within the proposed approach a wide variety mechanistic, kinetic and
thermodynamic aspects of electrocatalytic reactions can be addressed on equal footing
within GCE. Initial demonstration of the theory on Au-catalyzed Volmer reaction
demonstrates a proof-of-method for the computational approach as well as accuracy
and predictivity of the theory for adiabatic reactions.

The advances herein enable computational studies to e.g. address tunnelling
pathways and non-adiabaticity electrochemical reactions kinetic and mechanisms.
Understanding and controlling (non-adiabatic) tunneling can open up new reaction
pathways to avoid constraining scaling relations[160, 161, 162] encountered for adiabatic
PCET reactions. Besides applications, the advanced rate theories will improve fundamental understanding of electrochemical kinetics in e.g. de-coupled and non-adiabatic ET, PT, and PCET. This contributions are especially important for weakly-binding catalysts, but neglected in computational studies thus far.

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9. Declaration of interest

Declarations of interest: none

10. References

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Supporting information for ”Grand canonical rate theory for electrochemical and electrocatalytic systems I: General formulation and proton-coupled electron transfer reactions”

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1. Problem of combining "orbital-based" rate theories and first principles methods: Choosing localized empty and filled orbitals

1.1. Orbital based electron transfer rate theories

There are two commonly used orbital-based approaches for describing charge transfers rate at electrode surfaces. The first one was developed by Dogonadze, Levich, and Kutznetsov (DLK)[1], who assumed a weak interaction between the donor and the acceptor. Their treatment yields an expression similar to Marcus theory and the model goes by various names including Marcus-Hush-Chidsey[2], Gerischer[3], Marcus-DOS[3] or just the density-of-states (DOS) model. In the case of a metallic electrode, the molecular orbitals interact with a continuum of electronic states from the metal and therefore one needs to integrate over all the metallic bands. An implicit assumption in the DOS model is that charge transfer takes place between two one-electron orbitals rather than two many-electron wave functions. Also, the effect of the electrode potential $E$ is assumed to linearly change the occupation of orbitals without otherwise changing the one-electron levels. For electrochemical charge transfer reactions require information only on the molecular orbital $\epsilon_0$ and its DOS $\rho_0(\epsilon_0)$ and (quasi-continuum) of electrode bands $\epsilon$ with DOS $\rho(\epsilon)$. In this case the charge transfer is [1, 4] (see also 1)

$$k_{DOS}(E) = \int d\epsilon W(\epsilon, \epsilon_0) f(\epsilon - E) \rho(\epsilon) \rho_0(\epsilon_0) \quad (1)$$

where $W$ is the transition probability and $f$ is the Fermi-Dirac distribution. Originally, the DLK model was derived for the weak interaction limit and harmonic energy surfaces in which case the result is well-known [1, 4]

$$k_{DOS}(E) \approx \sqrt{\frac{\beta}{4\pi\lambda}} \int_{-\infty}^{\infty} d\epsilon |H_{ab}(\epsilon, \epsilon_0)|^2 f(\epsilon - E) \exp \left[ -\beta \left( \lambda + \epsilon_0 (E^0 - E) - \epsilon_0 \right)^2 \right] \quad (2)$$

$H_{ab}(\epsilon, \epsilon_0) = \langle \psi_\epsilon^a | \hat{H} | \psi_\epsilon^b \rangle$ denotes the Hamiltonian matrix element between the molecule and electrode orbitals corresponding to energy levels $\epsilon_0$ and $\epsilon$, respectively, in the initial $a$ and final $b$ diabatic states. $E$ is the electrode potential and $E^0$ is the formal equilibrium potential. Depending on the model used for the reactant DOS, the weakly interacting limit by Dogonadze, Gerischer’s model with a Gaussian dependency or Schmickler’s model (see below) maybe obtained as shown in Ref. [5]

The other approach is due to Schmickler[6, 7] and has been dubbed as the potential energy curve (PEC) method[5]. The PEC method applies a modified Newns-Anderson (N-A) Hamiltonian for building the PECs
Figure 1. Conventional (left) and GCE Marcus theory (right). The conventional theory is based on transitions between single-electron orbitals while the current GCE framework utilized general many-electron wave functions.

\[ H_{N-A} = \epsilon_0 n_0 + \sum_k \epsilon_k n_k + \sum_k (v_{k0} c_k^\dagger c_r + v_{r+k} c_0^\dagger c_k) + \frac{1}{2} \sum_i \hbar \omega_i (p_i^2 + q_i^2) + (n_0 - z) \sum_i (\hbar \omega_i g_i q_i) \]

where the terms describe reactant orbital, orbitals of the electrode, electron exchange terms using coupling matrix elements \( v \), harmonic bath at frequencies \( \omega_i \), momenta \( p_i \) and coordinate \( q_i \) while the last term couples the reactant at charge state \( z \) to the harmonic bath. Connecting the initial and final states of the redox reaction along a charge transfer coordinate \( r_q \) and using N-A Hamiltonian, the PEC is

\[ u(r_q, \epsilon_F) = \frac{r_q^2}{4\lambda} + (\epsilon_0 + r_q - \epsilon_F) \langle n(r_q) \rangle + \frac{\Delta}{2\pi} \ln[(\epsilon_F - r_q - \epsilon_0) + \Delta^2] \]

where \( \langle n(r_q) \rangle = 1/2 + 1/\pi \tan^{-1}((\epsilon_F - r_q - \epsilon_0)/\Delta) \) is the charge at \( r_q \) and \( \Delta(\epsilon') = \pi \sum_k |v_{0,k}|^2 \delta(\epsilon' - \epsilon_k) \) is the effective coupling constant. Then, the charge transfer barrier is \( u^t = u(r_q = r_{\text{max}}, \epsilon_F) - u(r_q = 0, \epsilon_F) \) and the rate is

\[ k_{PEC} = \kappa \exp[-\beta u^t] \]

At the weak interaction limit, both the DOS and PEC models are in their essence formulations of Fermi’s Golden rule describing electron transfer between single electron orbitals.[7]
1.2. Orbital based Fermi Golden rule formulation

Here a modern and general Golden rule is revisited to discuss inherent limitations of the orbital-based formulation. For this purpose the initial (final) state at the initial (final) geometry can be approximated by a single diabatic electronic state $\Psi(R_{\text{initial}}) \approx |\psi_I\rangle |\chi_j\rangle$ and using the Hamiltonian in Eq. (6). A similar equation can also be written for adiabatic states as shown in Ref. [8, 9]. In the diabatic Fermi Golden rule formulation the Hamiltonian is [10, 11]

$$\hat{H}_{el} = \sum_i E_i^I |I_i\rangle \langle I_i| + \sum_f E_f^F |F_f\rangle \langle F_f| + \sum_{if} \Delta_{if} (|I_i\rangle \langle F_f| + |F_f\rangle \langle I_i|)$$

(6)

where $|K^k\rangle = |\psi_k\rangle |\chi_k\rangle$ is a vibronic wave function consisting of $|\psi_k\rangle$, a one electron orbital and $|\chi_j\rangle$ a nuclear wave function. Reaction rates are computed using the general flux formulation presented in the main article with the following transition probability and flux [10, 11]:

$$P(E) = \frac{1}{2(2\pi \hbar)^2} \text{Tr} \left[ \hat{F} \delta(E - \hat{H}_N) \hat{F} \delta(E - \hat{H}_N) \right]$$

and $\hat{F} = 1/\hbar \Delta |0\rangle \langle 1| + |1\rangle \langle 0|$, respectively. $\Delta_{if}$ is a general diabatic coupling term, which in the Franck-Condon approximation is

$$\Delta_{if} = |\langle \psi_f | V | \psi_i \rangle|^2 \sum_{kl} |\langle \chi_k | \chi_l \rangle|^2$$

(7)

Following standard thermalized Fermi-golden rule derivation [12, 10, 11] for a transition between two electronic states gives

$$k_{i \rightarrow F} = \frac{2\pi}{\hbar} \sum_{i \in I, f \in F} k_{i \rightarrow f}$$

(8a)

$$k_{i \rightarrow f} = \frac{|V_{if}|^2}{\sum_l \exp[-E_{i,l}]} \sum_{tk} \exp[-E_{i,t}] |\langle \chi_k | \chi_l \rangle|^2 \times \delta(E_i - E_f + E_t - E_k)$$

(8b)

$$= |V_{if}|^2 F(E_i - E_f)$$

where $F(E_i - E_f)$ is the thermally averaged Franck-Condon factor (see Section 9 of the SI). If the nuclear wave functions are taken to be those of a harmonic oscillator, the Marcus barrier and the rate constant can be obtained from the derivation in Section 3 of the SI. Note that transition between all one electron orbitals are considered here.

To obtain the DOS-model for electron transfer, only a subset of the transition rates is considered. Intuitively, for an reduction of a molecule, transitions from the localized
occupied metal orbitals to empty orbitals localized at the molecule should be considered. This leads to

\[ k_{\text{red}} = \frac{2\pi}{\hbar} \sum_{i \in \text{filled}} \sum_{f \in \text{empty}} k_{i \rightarrow f} = \frac{2\pi}{\hbar} \sum_{f \in \text{empty}} \int d\epsilon \rho(\epsilon) f(\epsilon - \epsilon_F) k_{i \rightarrow f} \] (9)

where the second equation highlights the close correspondence with the DOS method (Eq. (1)), \( \rho(\epsilon) \) is the DOS and \( f \) the Fermi-Dirac distribution. Note also that the PEC method uses a Hamiltonian similar diabatic Hamiltonian here. In PEC the total transition probabilities from initial to final state are also computed using orbital-to-orbital formulation described above.

1.3. Choosing the orbitals

Both DOS and PEC share a fundamental open question: how does one choose the localized and empty/filled orbitals? This situation is faced in a typical first-principles calculations, where (canonical) one electron orbitals are highly delocalized even when charge-localized diabatic states are used, making the choice of active orbitals difficult. An important result learned from orbital localization methods\[13, 14, 15, 16\] is that the energy from a single determinant method such as DFT or Hartree-Fock methods is invariant to orbital rotation within the occupied molecular orbitals. Thus, occupied orbitals can be localized using a unitary rotation which leaves the energy, and the total wave function unchanged; during this process the spatial shape and spread of filled one electron orbitals are drastically changed. Also, the empty, virtual orbitals can be localized separately. However, the filled and empty are not allowed to mix during the localization to avoid changes in occupation of numbers\[17\]. As mixing the unoccupied-occupied subspaces is forbidden, orbital localization is performed separately for the empty and filled orbitals and consequently two different unitary transforms are required.

A concrete example helps to understand why the orbital localization causes practical difficulties. Consider for example an outer-sphere ET from an electrode to \( \text{O}_2 \) forming a superoxide species. Here the initial state wave functions \( \{|I\rangle\} \) would be occupied orbitals localized on the metal and the final state orbitals \( \{|F\rangle\} \) would be empty states localized on \( \text{O}_2 \). After a normal DFT calculation, one performs a unitary transform on both the initial and final states separately such that the the orbitals are well localized to the molecule and metal for both states: \( |I\rangle = \hat{U} |I_{\text{DFT}}^{\text{filled}}\rangle \) and \( |F\rangle = \hat{V} |F_{\text{DFT}}^{\text{empty}}\rangle \), with \( \hat{U}\hat{U}^\dagger = 1 \) and \( \hat{V}\hat{V}^\dagger = 1 \). Note that nuclear wave function remain unchanged as the electronic energy is unaffected by the transformation. Thus, the unitary transformation leaves the thermally averaged Franck-Condon weight unchanged.

However, the electronic coupling elements for a given \( V_{if} = \langle i|\hat{H}|f\rangle \) change drastically as the electronic orbitals are rotated. This is easily seen from the close
correspondence\[18\] between the coupling and overlap elements \( \langle i|V|f \rangle \approx v \langle i|f \rangle \), where \( v \) is a constant. Changing from the localized to delocalized states is written as \( \langle i|f \rangle = \langle i_{\text{dft}}|\hat{U}^\dagger\hat{V}|f_{\text{dft}} \rangle \neq \langle i_{\text{dft}}|f_{\text{dft}} \rangle \) when final (empty) and initial (filled) canonical DFT orbitals are localized separately. Only when \( \hat{U} = \hat{V} \) is the overlap between the localized and canonical orbitals the same; this would require of mixing of the filled and empty canonical orbitals resulting in changes in the total energy and the total wave function and is therefore discouraged.

As a concrete example consider Eq. (9) where only states below the Fermi-level contribute to the reduction rate. As potential is changed, some orbitals become empty or occupied changing the driving force of the reaction which remains unchanged under the orbital localization. The rate is dictated by transition probability directly related to the matrix elements in non-adiabatic reactions. Thus, the rate of non-adiabatic electron transfer reaction depends on how the orbitals are chosen and localized. This can lead to inconsistent and incorrect interpretation of the electrochemical rate as a function of the potential if basic single determinant methods are used to parametrize the DOS or PEC models. Great care is needed when the methods and as emphasized in Ref. [19] “this is not a failure of the computational methods used but is a consequence of how the rate constant is defined by the phenomenological equations. It is therefore important to choose the approach which is equivalent to the experiment or thought experiment that the theory is attempting to reproduce”.

Based on the above discussion, a very important conclusion is reached: the rate obtained from the orbital-based Fermi golden rule, DOS or PEC using only the ”active orbitals” depend on the way the orbitals are localized. Therefore, one needs to acknowledge that orbital localization needed when the orbital-based models are parametrized using canonical DFT methods, leads to arbitrary changes in the rate constant depending on the localization or rotation used scheme. Hence, while the energy, density, and the total wave function remain unchanged after a unitary transformation of the orbitals, single orbitals and single orbital overlaps will necessarily be affected. Therefore, a unitary transformation such as orbital localization will unphysically affect the rate obtained from methods using one-electron orbitals and orbital-to-orbital transitions to compute the transition probability. If one electron-based the DOS or PEC methods are parametrized using first-principles approaches, methods such as fragment orbital DFT\[20\] methods might be applicable.

Care is also required when using many-body wave functions for computing the rates. While unitary transform does not change any observables of a single diabatic wave function, the off-diagonal matrix elements might be sensitive to orbital rotations. However, in approaches such constrained DFT employed in this work, the coupling elements are functionals of the electron densities of the initial and final state\[21\] and as such in principle unaffected by orbital localization.
2. Grand canonical formulation for thermodynamics of electrochemical systems

Below the necessary details for grand canonical formalism are presented. A more complete treatment is given in Ref. [22].

Within GCE all expectation values are computed using

$$\langle O \rangle = \text{Tr} \left[ \hat{\rho} \hat{O} \right]$$

with the grand canonical density operator

$$\hat{\rho} = \frac{\exp\left[-\beta(\hat{H}_{\text{tot}} - \sum_i \hat{\mu}_i \hat{N}_i)\right]}{\text{Tr}\left[\exp\left[-\beta(\hat{H}_{\text{tot}} - \sum_i \hat{\mu}_i \hat{N}_i)\right]\right]}$$

where $\hat{H}_{\text{tot}}$ is the Hamiltonian, $\hat{\mu}_i$ is the electrochemical potential of species $i$, and $\hat{N}$ is the number operator. The partition function is defined as $\Xi = \text{Tr}\left[\exp\left[-\beta(\hat{H}_{\text{tot}} - \sum_i \mu_i \hat{N}_i)\right]\right]$ from which the grand free energy is $\Omega[T, V, \mu] = -k_B T \ln \Xi = E - TS - \sum_i \mu_i \hat{N}_i$. The probability of being in microstate $i$ is

$$p_{GC}^i = \frac{\exp\left[-\beta \langle \Psi_i | \hat{H}_{\text{tot}} - \sum_j \hat{\mu}_j \hat{N}_j | \Psi_i \rangle\right]}{\Xi}$$

In the above equation, $|\Psi_i\rangle$ is the total wave function of both the electrons and nuclei so that the particle number operators $\hat{N}_i$ corresponds to electrons or the nuclear identities as specified below. With these definitions fixed potential, grand canonical can be computed. For example, the grand energy for electrons $n$ and electrolyte $\pm$ with fixed chemical potential is given by

$$\Omega(T, V, \mu_\pm, \mu_n) \equiv \sum_i p_i \left[ \beta \ln p_i + \langle \Psi_i | \hat{H}_{\text{tot}} - \mu_\pm (\hat{N}_+ + \hat{N}_-) - \mu_n \hat{N}_n | \Psi_i \rangle \right]$$

$$= \text{Tr}\left[\hat{\rho} \hat{\Omega}\right] \equiv \Omega[\hat{\rho}]$$

3. Adiabatic and non-adiabatic harmonic TST rates

Here classical harmonic TST (HTST) for adiabatic and non-adiabatic reactions within GCE are derived.

3.1. GCE-TST with classical nuclei

For classical nuclei, the general rate equation in the GCE is written in terms of the time-integral of the flux correlation function contains all the dynamic information[23, 11]:

$$P_r(p, q) = \lim_{t \to \infty} h[f(q_t)] = \int_0^\infty dt \frac{d}{dt} h[f(q_t)] = \int_0^\infty dt C_{ff}(q_t, p_t).$$

With this definition the classical TST rate is
\[ k(T, V, \mu) \Xi_I = \sum_{N=0}^{\infty} \exp[\beta \mu N] \int \exp[-\beta E] dE P_{cl}(E) \]

\[ = \sum_{N=0}^{\infty} \exp[\beta \mu N] \int \frac{d\mathbf{p} \mathbf{q} \exp[-\beta H(p, q)] F(p, q) P_{cl}(p, q)}{(2\pi \hbar)^N} \]

\[ = \sum_{N=0}^{\infty} \exp[\beta \mu N] \int \frac{d\mathbf{p} \mathbf{q} \exp[-\beta H(p, q)] F(p, q) \int_0^\infty dt C_{ff}(t)}{(2\pi \hbar)^N} \]

\[ \approx \sum_{N=0}^{\infty} \exp[\beta \mu N] \frac{k_B T}{\hbar} Q^\dagger \int dt \delta(t) = \sum_N \exp[\beta \mu N] \frac{k_B T}{\hbar} Q^\dagger \]

\[ \equiv \frac{k_B T}{\hbar} \Xi^\dagger \]

where on the second last line making the short time approximation\[23\] to \( C_{ff}(t \to 0) = \frac{k_B T}{\hbar} Q^\dagger \delta(t) \) leads to the TST expression.

### 3.2. Adiabatic HTST

The general TST rate equation is shown in Eq. 5 of the main article. First, consider a general case where potential the number of both nuclei and electrons is allowed to fluctuate. Usually, for \( N_N \) classical nuclei the Hamiltonian in mass-weighted coordinates \((x_i)\) and momenta \( P_i \) is written as

\[ H_{cl} = \sum_{i \in N_N} P_i^2 + V(x_i) \]

\( V(x_i) \) defines the (Born-Oppenheimer) potential energy surface.

Then consider a system is open to electrons at a fixed electron chemical potential while number of nuclei is fixed. Also, the system is assumed adiabatic meaning that the number and distribution of electrons adjusts instantaneously to the nuclear configuration. This is the common situation considered in first principles calculations at fixed electrode potential calculations. For this case, the Kohn-Sham-Mermin theorem guarantees that electronic energy and distribution are unique to a given electron chemical potential and external potential (here provided by the nuclei). Hence, the potential energy \( V \) is not only a parametric function of the nuclear positions but also the chemical potential of the electrons. Furthermore, as shown in Ref. [22], the grand free energy of the electrons is given by \( \Omega_n(T, V, N_N, \mu_n; x_i) \). As the nuclei move the on the effective potential energy surface provided by the electrons, one recognizes that \( V(x_i, \mu_n) = \Omega_n(T, V, N_N, \mu_n; x_i) \) (see Ref. [22] and 2). Then, for the open electronic system, the classical Hamiltonian for the nuclei is

\[ H(N_N)_{cl} = \sum_{i \in N_N} P_i^2 + V(x_i, \mu_n) \equiv H_{cl} \]

where \( I \) and \( \dagger \) denote the initial and transition states. The TST rate is written as [12]
\[ \begin{align*}
  k_{TST}(N, V, T) Q_I &= \int_N dP \int_N \mathbf{d}x \exp \left[ -H_{cl}^I / \beta \right] \delta(f(x))(\nabla f \cdot P^N) h(\nabla f \cdot P^N) \\
  \text{where} f \text{ is the } N - 1 \text{ dimensional dividing surface between the reactants and products, } \nabla f \cdot P^N = P_{ni} \text{ is the momentum normal to } f \text{ identified as the reaction coordinate, } h(\nabla f \cdot P^N) = h(P_{ni}) = \text{a step function separating the reactant and product basins, and } \delta(f(x^N)) \text{ restricts the geometries to lie on the dividing surface. With these definitions the canonical HTST at fixed electron chemical potentials follows from:}
\end{align*} \]

\[ k_{HTST}(T, V, N) = \int_N dP \int_{N-1} \mathbf{d}x P_{ni} \frac{\exp \left[ -H_{cl}^I / \beta \right]}{Z_I} = \frac{1}{\sqrt{2\pi\beta}} \int_N \mathbf{d}x \exp \left[ -\beta V(x_i, \mu_n) \right] \approx \frac{v_N}{\sqrt{2\pi}} \frac{\prod_{i=0}^{N-1} v_i}{\prod_{i=0}^{N-1} v_i^\dagger} \exp \left[ -\beta (\Omega_n^I - \Omega_n^I) \right] = \frac{v_N}{2\pi} \exp \left[ -\beta (\Omega_n^I - \Omega_n^I) \right] = \frac{v_N}{2\pi} \frac{\exp \left[ -\Delta \Omega_n^I \beta / 2 \right]}{2\pi} \]

where at the second last row the effective potentials are Taylor expanded in terms of normal mode coordinates with corresponding frequencies \( v_i \) and \( v_N \) is the frequency along the reaction coordinate: \( V^I / I = \Omega_n^I + 1/2 \sum_i v_i q_i^2 \). The last equality follows from setting the nuclear vibrational entropy \( S_n = k_B \ln \left( \prod_{i=0}^{N-1} v_i / \prod_{i=0}^{N-1} v_i^\dagger \right) \) and setting the total grand free energy to \( \Omega_n = \Omega_n - TS_n \). Here the subscript \( N \) reminds that the number of nuclei was kept fixed above. Note that Eq. (17) would be used in typical first principles calculations at fixed electrode potentials where the electron chemical potential and number of nuclei are fixed.

The above treatment can also be extended to treat situations in which both the number of electrons and nuclei are allowed to fluctuate. This is straight-forward and can be obtained by. Inserting Eq. (17) in Eq. 5 of the main paper and applying Eq. 6 of the main paper leads to

\[ k_{HTST}(T, V, \mu) = \frac{\langle v_N \rangle}{2\pi} \frac{\exp \left[ -\Delta \Omega_n^I \beta / 2 \right]}{2\pi} \]

where \( \langle v_N \rangle \) is the effective frequency along the reaction coordinate computed using effective fixed potential PESs.
3.3. Non-adiabatic HTST

Next, non-adiabatic harmonic transition state theory (NA-HTST) approximation to the rate is developed. Unlike for the canonical case, only a fixed number of nuclei is treated. NA-HTST also requires the calculation of matrix elements $H_{AB} = \langle \Psi_A | \hat{H} | \Psi_B \rangle$. These $H_{ABs}$ are defined only when $|\Psi_A\rangle$ and $|\Psi_B\rangle$ have the same number of both electron and nuclei. Also, the adiabatic approximation cannot be used and the electrons do not instantaneously adapt to nuclear positions. Hence, unlike for the adiabatic case, constant electron number $V(x,n)$ rather than constant electron potential $V(x,\mu_n)$ is used. The appropriate Hamiltonian is given by Eq. (6), in which $H_d = \sum_{i \in N} \frac{P_i^2}{2m_i} + V_i(x_i)$.

Using this Hamiltonian, assuming a quadratic potential $V$ and applying the Golden rule form the basis for NA-HTST. This derivation can be found in e.g. Ref [24]. Another path, presented below, is to use the classical transitions state theory using the Landau-Zener transition $P_r$ probability[25, 12] and assuming that the potential energies are quadratic. Then, the following identities are used: The reorganization energy and vibrational frequency along the reaction coordinate are related as $\lambda = 2v_N^2 \Delta q^2 = 2mv_N^2 \Delta x^2$, where $\Delta q$ and $\Delta x$ are the geometric differences of the initial and final states in mass weighted and cartesian coordinates states, respectively. The differences of forces can written as gradient of the two parabolas at the transition state as shown in Ref. [24] to yield $|\Delta F|_\parallel = \lambda/\Delta x$. With these definitions, fixed number (canonical) electronic/nuclear NA-HTST can be derived:
\[ k_{\text{HTST}}^n(T, V, N, N_n) = \int_N dP \int_{N-1} dP_n P_n^{\dagger} \frac{\exp[-H^{\dagger}_d/\beta]}{Z_I} \]

\[ = \int_N dP \int_{N-1} dx \left( 1 - \exp \left[ -\frac{2\pi |H_{IF}|^2}{\hbar |P_n^{\dagger} \nabla_{n^{\dagger}} (V_I - V_F)|} \right] \right) P_n^{\dagger} \frac{\exp[-H^{\dagger}_d/\beta]}{Z_I} \]

linearize exp 
\[ \approx \int_N dP \int_{N-1} dx \frac{2\pi |H_{IF}|^2}{\hbar |P_n^{\dagger} \Delta F|} P_n^{\dagger} \frac{\exp[-H^{\dagger}_d/\beta]}{Z_I} \]

forces 
\[ = \int_N dP \int_{N-1} dx \frac{2\pi |H_{IF}|^2}{\hbar |P_n^{\dagger} \Delta F|} \frac{\exp[-H^{\dagger}_d/\beta]}{Z_I} \]

integrate 
\[ \approx \frac{2\pi |H_{IF}|^2}{\hbar |\Delta F|} \int_N dx \exp[-V_{IF}/\beta] \]

harmonic TST 
\[ \approx \sqrt{2\pi \frac{|H_{IF}|^2}{\hbar |\Delta F|}} v_N \prod_{i=1}^{N-1} v_i \exp[-(E^{\dagger}_i - E_i)/\beta] \]

vib. entropy 
\[ = \sqrt{2\pi \frac{|H_{IF}|^2}{\hbar |\Delta F|}} v_N \exp[-\Delta A^{\dagger} / \beta] \]

\[ |\Delta F|_{i=\lambda/\Delta x} \approx \sqrt{2\pi \frac{|H_{IF}|^2}{\hbar |\Delta F|}} \sqrt{\frac{m v_N |\Delta x| |H_{IF}|^2}{\hbar^2 \lambda}} \exp[-\Delta A^{\dagger} / \beta] \]

\[ \lambda = \frac{2mv_N^2 |\Delta x|^2}{\hbar^2 \lambda} \approx \sqrt{\frac{\pi \beta}{\hbar^2 \lambda}} |H_{IF}|^2 \exp[-\Delta A^{\dagger} / \beta] \]

Marcus barrier 
\[ \approx \sqrt{\frac{\pi \beta}{\hbar^2 \lambda}} |H_{IF}|^2 \exp \left[ -\beta \frac{(\Delta \Omega + \Lambda)^2}{4\Lambda} \right] \]

\[ \text{(19)} \]

The above rate is derived for fixed number of electrons and nuclei. As done for the adiabatic case, this fixed particle rate needs to be turned to a fixed potential rate. In particular, the electronic subsystem needs to be open in order to study kinetics at a fixed electrode potential. However, generalization of the NA-HTST to GCE is significantly more difficult compared the the adiabatic as discussed. The electronically GCE NA-HTST can be accomplished the approach in Section 4 of the main paper.

To gain more insight, it is useful to compare the above derivation to the GCE-EVB picture used for deriving the GCE equivalent of Marcus barriers and Landau-Zener transmission probability. These consideretations directly lead to the hybrid NAGCE-EVB rate constant

\[ k_{\text{NAGCE-EVB}}(T, V, N, \mu_n) \approx \left\langle \sqrt{\frac{\pi \beta}{\hbar^2 \lambda}} |H_{IF}|^2 \right\rangle_{\mu_n} \exp \left[ -\beta \frac{(\Delta \Omega + \Lambda)^2}{4\Lambda} \right] \]

\[ \text{(20)} \]

where the prefactor is computed for either i) some particle number and assumed to independent of the electrode potential or ii) various particle numbers and weighted according to the grand canonical distribution.
4. Effective grand canonical diabatic states using density matrices

Here the theoretical and technical details of the GCE-EVB theory are presented. To form the GCE diabatic states, the work of Reimers[8, 9] on canonical ensembles is followed. As noted by Reimers, the density matrix \( \hat{\rho} \) can be written using either adiabatic or non-adiabatic states. Especially, when only two electronic states are used, the connection of the Born-Huang expansion bears striking resemble to the commonly used \( 2 \times 2 \) diabatic Hamiltonians used for deriving electron transfer rate theory. In the canonical ensemble, the diabatic states are \( \phi_I \) and \( \phi_F \) corresponding to the electron localized on the initial (I) or final (F) state while the molecular electronic-vibrational Hamiltonian is

\[
H_{dia}(N, V, T) = \begin{bmatrix}
H_{II} & H_{IF} \\
H_{FI} & H_{FF}
\end{bmatrix}
\]

(21)

with

\[
H_{II}(R) = \langle \phi_I | \hat{H}_{el}(R) | \phi_I \rangle + \hat{T}_{nuc} = E_I + \hat{T}_{nuc}
\]

(22a)

\[
H_{FI} = H_{IF} = \langle \phi_I | \hat{H}_{tot}(R) | \phi_F \rangle
\]

(22b)

\[
H_{FF} = \langle \phi_F | \hat{H}_{el}(R) | \phi_F \rangle + \hat{T}_{nuc} = E_F + \hat{T}_{nuc}
\]

(22c)

where \( \hat{T}_{nuc} \) is the nuclear kinetic energy operator, \( \hat{H} = \hat{H}_{el} + \hat{T}_{nuc} \), and \( \hat{H}_{el} \) includes electron kinetic energy and Coulomb energies of the electron-nucleus system. The Born-Huang, or vibronic, states are

\[
\Psi_i(R) = \sum_j [C_{ij}^I | \psi_I \rangle | \chi_j \rangle + C_{ij}^F | \psi_F \rangle | \chi_j \rangle]
\]

= \sum_{k=I,F} | \psi_k \rangle \sum_j C_{ki,j}^I | \chi_j \rangle
\]

(23)

where \( \Psi \), \( \psi \), and \( \chi \) are the vibronic, electronic, and nuclear wave functions, respectively. \( C \) is the weight of each state. Using these definitions the, the canonical ensemble density matrix is

\[
\rho(N, V, T) = \begin{bmatrix}
\rho_{II} & \rho_{IF} \\
\rho_{FI} & \rho_{FF}
\end{bmatrix}
\]

(24)

with \( \rho_{AB} = \sum_j C_{ji}^A C_{ji}^B \) and the total density matrix has dimension \( (2 \times N_i) \times (2 \times N_i) \).

Next the diabatic canonical Hamiltonian is generalized to the grand canonical ensemble. To simplify the notation, it is assumed that the initial and final can approximated as a single electronic state and a single vibrational state - extension to include more vibrational state is straight-forward. Then, the total vibronic state is written as \( \Psi(R) \approx c_I | \psi_I \rangle | \chi_I \rangle + c_F | \psi_F \rangle | \chi_F \rangle \). In electron transfer theory the vibronic
Supporting Information

states are often assumed to be harmonic but here such an assumption is not needed. Next, the total number of electrons is allowed to fluctuate while the electron Fermi-level is fixed. These are effectively introduced by using the equilibrium reduced density operator within the GCE [22] (see also 2)

\[
\hat{\rho}_{\text{red}} = \sum_N p_N \sum_{ij} |\Psi_{Ni}\rangle \langle \Psi_{Nj}|
\]

with

\[
|\Psi_i\rangle = c_I |\psi_I\rangle |\chi_I\rangle + c_F |\psi_F\rangle |\chi_F\rangle
\]

where \(p_N\) is the GCE weight for a state with \(N\) electrons. The resulting density matrix will have \(N\)-dimensional block-diagonal form with \(2 \times 2\) blocks. Similarly the Hamiltonian matrix is made of Eq.(21) \(H_\text{dia}^N\) blocks. Diagonalizing each block separately will give canonical adiabatic states whereas Tr\[\hat{\rho}_{\text{red}}\hat{H}\] gives the adiabatic grand canonical free energy. Because the trace is cyclic, both \(\hat{\rho}_{\text{red}}\) and \(\hat{H}\) can be reorganized which keeps the (diabatic) free energy unchanged as long as diagonal elements remain at the diagonal. This freedom is utilized for reorganizing the density matrix so that the upper part of \(\hat{\rho}_{\text{red}}\) and \(\hat{H}\) correspond to the initial state and the lower part to the final diabatic states. Tracing the upper and lower parts separately, diabatic GC free energies of initial and final states (\(\Omega_{II}\) and \(\Omega_{FF}\)) are obtained. These states and their effective couplings are used in the main paper to derive the GCE-EVB model.

5. Grand canonical perturbation theory

Here it is shown how the needed GCE-EVB states rigorously defined and computed with grand canonical perturbation theory. To keep the present work as general as possible i.e. allowing both the number of electron and nuclear species to fluctuate, a simple effective Hamiltonian cannot be specified. Instead, explicit sampling of the GCE and number of electrons and nuclei is needed. In this case a novel extension of the canonical thermodynamic perturbation theory[26] to GCE is utilized. Along these lines, the canonical energy operator \(H = H_0 + V\) is defined and partitioned to contributions from the unperturbed \(H_0\) part and a perturbation \(V\). The total GC partition function \(\Xi\) and grand energy \(\Omega\) are given as (see Section 2)

\[
\Xi = \text{Tr}[H - TS - \mu N] \quad \text{and} \quad \exp[-\beta \Omega] = \Xi
\]

Then, the total grand energy can be multiplied and divided by the unperturbed grand energy

\[
\exp[-\beta \Omega] = \frac{\exp[-\beta(\Omega - \Omega_0)]}{\exp[-\beta \Omega_0]} = \frac{\exp[-\beta(\Omega_V)]}{\exp[-\beta \Omega_0]} = \langle \exp[-\beta V] \rangle_0 \tag{27}
\]
where the last identity means that the perturbation part of the grand energy is obtained with GCE sampling of the perturbation. For electron transfer reactions, the total Hamiltonian can be written as \[27\]

\[ H = K + U + V_x \]  

(28)

where \( K \) is the kinetic energy, \( U \) is the interaction energy and \( V_x \) is the perturbation which depends on extent of the reaction: \( x = 0 \) and \( x = 1 \) correspond to initial and final states, respectively. A linear switch from the initial to the final state is obtained using a switching potential \( V_x = V_I - x(V_F - V_I) \). This potential defines the initial and final diabatic states and based on the energies of the initial and final states \( E_I \) and \( E_F \). Furthermore, one defines the instantaneous energy gap \( \Delta E(R) = E_F(R) - E_I(R) = X \) at geometry \( R \). As noted by Zusman\[28\] and Warshel\[29\] (see also Ref. [30] for a combined discussion), the energy gap coordinate is directly related to the (solvent/bath) reorganization coordinate and both are often used in deriving electron transfer rates. It was recently shown by Jeanmairet et.al.\[27\] that the energy gap coordinate is a valid reaction coordinate also within GCE.

Combining the two-state GCE diabatic model for the initial \( I \) and final \( F \) states with the general perturbation result leads to

\[
\exp[-\beta\Delta\Omega] = \frac{\langle \exp[-\beta V_F] \rangle_F}{\langle \exp[-\beta V_I] \rangle_I} = \frac{\Xi^F}{\Xi^I} \tag{29}
\]

which results in \( \Delta\Omega = -\beta^{-1}\ln(\Xi^F/\Xi^I) \). Next, the sampling is constrained to a specific region of the energy gap. As recently shown in Ref. [27], a one-to-one mapping exists between the vertical energy gap \( \langle \Delta E \rangle_x \), \( x \), the potential \( V_x \), and the probability \( (p_x) \) of being in microstate sampled from the GCE: \( x \leftrightarrow \langle \Delta E \rangle_x \leftrightarrow V_x \leftrightarrow p_x \). Introducing the energy gap coordinate and noting that the energies of \( I \) and \( F \) are computed from the same Hamiltonians except for the ”perturbation” part allows writing

\[
\Delta\Omega = -\beta^{-1}\ln \left( \frac{\sum_N e^{\beta\mu N} \int dP^N dR^N e^{-\beta\Delta E+V_I}}{\sum_N e^{\beta\mu N} \int dP^N dR^N e^{-\beta V_I}} \right) = -\beta^{-1}\ln \langle e^{-\beta\Delta E} \rangle_I = \beta^{-1}\ln \langle e^{\beta\Delta E} \rangle_F \tag{30}
\]

where \( \Delta E = V_F - V_I \) is used. One can also obtain a probability distribution for the energy gap by performing constrained sampling\[12\] of the grand energy curves

\[
\Xi^i(X) = \sum_N e^{\beta\mu N} \int dP^N dR^N e^{-\beta E_i} \delta(\Delta E(R) - X) \tag{31a}
\]
Supporting Information

\[ p^i(X) = \frac{\Xi^i(X(R))}{\Xi^i} = \langle \delta(\Delta E(R) - X) \rangle_i = \frac{\sum_N e^{\mu N} \int dR^N dP^N \delta(\Delta E(R) - X) e^{-\beta E_i}}{\sum_N e^{\mu N} \int dR^N dP^N e^{-\beta E_i}} \]  

(31b)

so that \( \Xi^i = \int dX \Xi^i(X) \equiv e^{-\beta \Omega^i} \) and \( \Omega^i(X) = -\beta^{-1} \ln(p^i(X)) + \Omega^i \). Above \( \Omega^i \) is the diabatic grand energy and \( i = I \) or \( F \). Using the last identity and observing that integration over the probability is unity one obtains

\[ \Omega^i = -\beta^{-1} \ln \int dX e^{-\beta \Omega^i(X)} \]  

(32)

An important identity linking the diabatic grand energies to the energy gap is obtained by using the energy gap as the reaction coordinate. In this case the constrained grand energy along the energy gap leads to

\[ \Omega_I(\Delta E) = -\beta^{-1} \ln(\Xi_I(\Delta E)) = -\beta^{-1} \ln \left( \sum_N e^{\mu N} \int dP^N dR^N e^{-\beta E_i(RN)} \delta(\Delta E(RN) - \Delta E) \right) \]

\[ = -\beta^{-1} \ln \left( \sum_N e^{\mu N} \int dP^N dR^N e^{-\beta(E_F(RN) - \Delta E(R))} \delta(\Delta E(RN) - \Delta E) \right) \]

\[ = -\beta^{-1} \ln \left( e^{\beta \Delta E} \sum_N e^{\mu N} \int dP^N dR^N e^{-\beta E_F(RN)} \delta(\Delta E(RN) - \Delta E) \right) \]

\[ = -\Delta E - \beta^{-1} \ln \left( \sum_N e^{\mu N} \int dP^N dR^N e^{-\beta E_F(RN)} \delta(\Delta E(RN) - \Delta E) \right) \]

\[ = -\Delta E + \bar{\Omega}_F(\Delta E) \]  

(33)

At this point all relevant free energy identities within the GCE corresponding to the commonly used identities used for deriving the canonical Marcus theory have been obtained.[31, 32, 33, 34, 35, 29, 36] Refs. [31, 32, 33, 34, 35, 29, 36] show various ways to obtain the iconic canonical Marcus rate constant. To arrive at the corresponding rate constant in the GCE, it is shown that detailed balance is satisfied. At the transition state the initial and final diabatic grand energies are equal which results in

\[ \Omega_I(\Delta E^\dagger) = \Omega_F(\Delta E^\dagger) \]

\[ \rightarrow -\beta^{-1} \ln(p_I(\Delta E^\dagger)) + \Omega_I = -\beta^{-1} \ln(p_F(\Delta E^\dagger)) + \Omega_F \]

\[ \rightarrow \frac{p_I(\Delta E^\dagger)}{p_F(\Delta E^\dagger)} = \exp[-\beta(\Omega_F - \Omega_I)] = \exp[-\beta \Delta \Omega_{FI}] \]  

(34)

which shows that detailed balance is satisfied. The diabatic grand energy surfaces are computed from the energy gap distribution[35]
The transition state can then be identified from the intersection of the relative grand energy curves: \( g_I(\Delta E^\dagger) = g_F(\Delta E^\dagger) \). Computing the reaction rate using the standard transition state theory expression gives

\[
\kappa_{IF} = \kappa \frac{\exp[-\beta g_I(\Delta E^\dagger)]}{\int d\Delta E \exp[-\beta g_I(\Delta E)]} = \kappa p_I(\Delta E^\dagger) \quad (36)
\]

showing that the reaction rate is determined by the energy gap distribution function \( p_I(\Delta E) = \langle \delta(\Delta E(R) - \Delta E) \rangle_I \) from Eq. (31). Note, that microscopic reversibility is satisfied by construction. To obtain the iconic Marcus rate within GCE, one may follow the perturbation theory route\[26, 35\] and perform a cumulant expansion on the energy gap distribution as was done also when deriving the GCE-NATST in this work in section Section 4 of the main paper. It has been shown in several previous studies\[35, 37, 32\] that the second order cumulant expansion results a Gaussian form for the energy gap distribution:

\[
p_I(\Delta E) = \frac{1}{\sqrt{2\pi} \sigma_I} \exp \left[ -\frac{(\Delta E - \langle \Delta E \rangle_I)^2}{2\sigma_I^2} \right] \quad (37)
\]

where \( \langle \Delta E \rangle_I \) is the energy gap expectation value in the initial state obtained from Eq. (31) and \( \sigma_I = \langle \langle \Delta E \rangle^2 \rangle_I - \langle \Delta E \rangle_I^2 \) is the gap variance. The Marcus relation is then obtain after standard manipulations\[32, 25\] by inserting these relations in Eq. (33) result in the GCE Marcus rate of Eq. 11 of the main paper.

6. Thermodynamic analysis of outer-sphere ET in macroscopic systems

Consider a general outer-sphere ET reaction \( e^-(M) + B(sol) \rightarrow B^-(sol) \) where an electron is transferred from the metal (M) to molecule B in the solution phase (sol). The equilibrium potential is \( E^{eq} \). Changing the potential from \( E^{eq} \) to \( E \) i.e. introducing the over-potential \( \eta = E - E^{eq} \) changes the electron energy by \( \Delta \mu_e = -\eta \) for the initial state. The energy of the final state changes as \( \Delta \mu_{sol}^{sol} = -F \Delta \phi_{sol}(\eta) \) where \( \phi_{sol} \) is the electrostatic potential in the solution phase. The reaction energy is changed by \( \Delta A = -[\Delta \phi_{sol}(\eta) - \eta] \). \( \Delta \phi_{sol}(\eta) \) depends roughly linearly on \( \eta \). Hence, \( \Delta A \approx a \times \eta \)

7. Fourier transform and cumulant expansion for ET reactions

Here it shown how the non-adiabatic rate constants are obtained from cumulant expansion to the energy autocorrelation function. First, the autocorrelation function is related to the delta function as
\[ \sum_{m,n} p_{imN} \left| \langle Nnf | \hat{V}_N | imN \rangle \right|^2 \delta(E_{imN} - E_{fnN}) \]

\[ = \frac{1}{2\pi\hbar} \sum_{m,n} p_{imN} \left| \langle Nnf | \hat{V}_N | imN \rangle \right|^2 \int dt e^{it(E_{imN} - E_{fnN})/\hbar} \]

\[ = \frac{1}{2\pi\hbar} \sum_{m,n} p_{imN} \langle fN | \hat{V}_N | iN \rangle \langle inN | \hat{V}_N | f mN \rangle \int dt e^{it(E_{imN} - E_{fnN})/\hbar} \]

\[ \approx \frac{1}{2\pi\hbar} \sum_{m,n} p_{imN} \left| \langle fN | \hat{V}_N | iN \rangle \right|^2 \int dt \langle mN | nN \rangle \langle nN | mN \rangle e^{it(E_{imN} - E_{fnN})/\hbar} \]

\[ = \frac{1}{2\pi\hbar} \sum_{m,n} p_{imN} V_{N,if}^2 \int dt \left| \langle nN | mN \rangle \right|^2 e^{it(E_{imN} - E_{fnN})/\hbar} \]

\[ = \frac{V_{N,if}^2}{2\pi\hbar} \int dt \left\langle e^{it(E_{imN}/\hbar)} e^{-it(E_{fnN}/\hbar)} \right\rangle \]

where \( C(t) \) is an energy autocorrelation function. The last two equations are amenable to two different ways of computing the rate constant. The last can be used with a cumulant expansion approach, while the second last has the form of a thermally averaged Franck-Condon treatment is presented in Section 9 of this supplement for completeness.

While nuclear quantum effects maybe important and can be included in the computation of \( C(t) \)[37], in the present work, nuclear degrees of freedom are treated classically. Following either Geva[37] or Marcus[38], the autocorrelation function can be expressed using a cumulant expansion[39]. Use of the second order cumulant expansion results in

\[ \langle \exp[iE_{fnN}t/\hbar] \exp[iE_{imN}t/\hbar] \rangle_i \approx \exp \left[ -\frac{it}{\hbar} \langle \Delta E_{f}^{N} \rangle - \frac{1}{\hbar^2} \int_0^\tau \int_0^{\tau_1} d\tau_1 \int_0^{\tau_2} d\tau_2 C(\tau_1 - \tau_2) \right] \]

where \( \langle \Delta E_{f}^{N} \rangle \) is the average free energy gap between the final and initial electronic diabatic states. Also \( C(\tau_1 - \tau_2) = \langle \delta \Delta E_{f}^{N}(\tau) \delta \Delta E_{f}^{N}(0) \rangle \) where \( \delta \Delta E_{f}^{N} = \Delta E_{f}^{N} - \langle \Delta E_{f}^{N} \rangle \). \( C(\tau_1 - \tau_2) \) is directly linked to the vibrational spectral density of the system[38, 40, 41, 12]. To obtain a manageable expression for the rate, the short time approximation or slow fluctuation limit[42] to the correlation function is used: \( C(\tau_1 - \tau_2) \approx C(0) = \langle \delta (\Delta E_{f}^{N})^2 \rangle \). Inserting this in Eq. (39) yields

\[ \exp \left[ -\frac{1}{\hbar^2} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 C(\tau_1 - \tau_2) \right] \approx \exp \left[ -\frac{t^2}{\hbar^2} \langle \delta (\Delta E_{f}^{N})^2 \rangle \right] \]

This is inserted in Eq. (38) to give
\[
\sum_{m,n} p_{imN} \left\langle Nnf | \hat{V}_N | imN \right\rangle \delta(E_{imN} - E_{fnN})
\]

\[
\approx \frac{V_{N,if}^2}{2\pi\hbar} \int_{-\infty}^{\infty} dt \exp \left[ \frac{it}{\hbar} \langle \Delta E_{fi}^N \rangle - \frac{t^2}{\hbar^2} \langle (\delta(\Delta E_{fi}^N))^2 \rangle \right]
\]

\[
= \frac{V_{N,if}^2}{2\pi\hbar} \sqrt{\frac{2\pi\hbar^2}{\langle \delta(\Delta E_{fi}^N)^2 \rangle}} \exp \left[ -\frac{\langle \Delta E_{fi}^N \rangle^2}{2\langle (\delta(\Delta E_{fi}^N))^2 \rangle} \right]
\]

\[
\approx \frac{V_{N,if}^2}{2\pi} \sqrt{\frac{\pi}{k_B T \lambda}} \exp \left[ -\frac{(\Delta E_{fi}^N + \lambda)^2}{4k_B T \lambda} \right]
\]

where on the last line it has been assumed that the free energy surfaces are quadratic along the energy gap coordinate. The reorganization and reaction energies are defined as \(\lambda = E_{im}(Q_F) - E_{in}(Q_I)\) and \(E_{fi}^N = E_{fn}^N(Q_F) - E_{im}^N(Q_I)\) (see Fig. 2 in the main paper).

A generalization to asymmetric GCE-diabatic energy curves can be made following Mattiat and Richardson\[24\]. Furthermore, it is assumed that the curvature of the quadratic surfaces is the same for all particle numbers \(N\) in which case the reorganization energy does not depend on \(N\). This should be to a rather good approximation as the reorganization is related to the reorientation of the surrounding medium which is expected be rather insensitive to the number of electrons in the system. For example, in the spin-boson model, which in the canonical ensemble yields the Marcus rate, the reorganization energy is only related to the bath frequencies in thermal equilibrium.\[12\]

If the spin-boson model is applied to the present GCE case, the vibrational, bosonic Hamiltonian would be assumed to be independent of the number of electrons and yield directly the reorganization energy which is independent of the number of particle for the GCE. The assumption that the reorganization energy is independent on the particle number can also be reinforced by doing a re-derivation of the rate using the thermalized Franck-Condon approach as shown in Section 9.

8. Grand canonical weights as a function of particle number

As shown in the main paper, computation of GCE rates involves a summation over states with different number of particles. To avoid the infinite summation, the crucial question is how many different states are in fact needed. This depends on the population probability or weight of different particle number states.

Here the weights as a function of \(\mu\) are studied for a graphene sheet. The graphene is modelled using small 4 atom unit cell repeated in the x and y directions. The vacuum along the z-directions is 15\(\text{Å}\). The GPAW\[43, 44, 45\] software is used for the DFT calculations. The grid spacing is set to 0.18\(\text{Å}\), 16 \(\times\) 16 \(\times\) 1 k-point is applied, and exchange-correlation effects are treated using the PBE\[46\] functional. The system is immersed in a continuum water solvent using the SCMVD model\[47\] using the standard
Supporting Information

| Charge | $\mu = -E_f$ | $E$ | $p(\mu = -4.03 \text{ eV})$ | $p(\mu = -3.06 \text{ eV})$ |
|--------|-------------|-----|----------------------------|----------------------------|
| -0.1   | -2.46       | -37.17 | 0.0096                     | 0.0536                     |
| -0.075 | -2.83       | -37.11 | 0.0349                     | 0.1203                     |
| -0.05  | -3.06       | -37.03 | 0.0988                     | 0.2102                     |
| -0.025 | -3.53       | -36.95 | 0.2148                     | 0.2825                     |
| 0      | -4.03       | -36.86 | 0.2973                     | 0.2417                     |
| 0.025  | -4.53       | -36.75 | 0.2144                     | 0.1077                     |
| 0.05   | -5.02       | -36.63 | 0.0971                     | 0.0301                     |
| 0.075  | -5.26       | -36.50 | 0.0335                     | 0.0064                     |
| 0.1    | -5.64       | -36.36 | 0.0089                     | 0.0010                     |

Table 1. Weights for different charge states of graphene as function of $\mu$, the electron chemical potential in eV. $E_f$ is the Fermi-level in eV, $E$ is the total energy, and $p$ are the weights.

parameters given in Ref.[47]. The charged systems are modelled using the homogeneous Poisson-Boltzmann model[22, 48] The weights are computed using the usual definition:

$$p_N = \frac{\exp[-\beta(E_N - \mu N)]}{\sum_N \exp[-\beta(E_N - \mu N)]} \quad (42)$$

The results are shown in Table 1. As can be seen the relevant weights for both $\mu_0 = -4.03$ and $\mu = \mu_0 \pm 0.5\text{eV}$ are captured by using 9 charge states. By carefully choosing the different charge states will reduce the number needed charge states. Furthermore, larger systems should require less states as these are ”closer” to the thermodynamic limit and the probabilities approach a Delta function as system size is increased.

9. Franck-Condon derivation of the non-adiabatic rate

The Franck-Condon treatment starts from the second-last line of Eq. (38) by noticing that

$$\frac{1}{2\pi\hbar} \sum_{m,n} p_{imN} V_{N,i}^2 \int dt |\langle nN|mN \rangle|^2 e^{it(E_{imN} - E_{fnN})/\hbar} = \frac{V_{N,i}^2}{2\pi} FC(\Delta E)_i \quad (43)$$

where $FC(\Delta E)_i$ is the thermalized Franck-Condon factor. In general case, the thermalized Franck-Condon factor can be computed by Fourier transforming it and using generating functions.[49] As shown in Ref. [42] chapter 6, the FC-factor can be written using the spectral density function $J_{fi}(\omega)$ to give
\[ FC(\Delta E)_i = \frac{1}{2\pi \hbar} \exp[G(0)] \int_{-\infty}^{\infty} dt \exp \left[ it \frac{\Delta E_{fi}^N}{\hbar} + G(t) \right] \]
\[ \approx \int_{-\infty}^{\infty} \frac{dt}{2\pi \hbar} \exp \left[ it \frac{\Delta E_{fi}^N - \lambda}{\hbar} \right] \exp \left[ -\frac{\lambda t^2}{\beta \hbar^2} \right] \]
\[ = \sqrt{\frac{1}{4\pi k_B T \lambda}} \exp \left[ -\frac{(\Delta E_{fi}^N + \lambda)^2}{4k_B T \lambda} \right] \]

where \( G(t) = \int_{0}^{\infty} d\omega \cos(\omega t)(1 + 2n(\omega))J_{IF}(\omega) - \sin(\omega t)J_{IF}(\omega) \)
\[ \approx \int_{0}^{\infty} d\omega \frac{(\omega t)^2}{\beta \hbar \omega} J_{IF}(\omega) - i \int_{0}^{\infty} d\omega \omega J_{IF}(\omega) \]

using the high-temperature approximation \( (1 + 2n(\omega) \approx 2k_B T \gg 1) \), slow-fluctuating Debye solvent assumptions, and \( \int_{0}^{\infty} d\omega J_{IF}(\omega) = \lambda/2 \). Hence, if the spectral density not sensitive to the number of electrons, the reorganization energy is independent on the number of electrons in the systems. For practical purposes this is expected to be a good approximation. When the approximate FC factor is introduced, Eq. (43) gives the Marcus rate in the GCE.

10. Decomposition of the reorganization energy to inner- and outer-sphere contributions

The total reorganization energy is often\[50, 51, 52, 53\] modified differentiate between inner- and outer-sphere contributions. This is achieved by partitioning the surrounding molecules to tightly bound ligands or inner-solvent solvent molecules and the bulk solvent. While this is not necessary in the approach taken in this work, separating the effect the nearby atoms or molecules and the solvent might be useful for a understanding the role of different constituents on the overall reaction. In both computational and theoretical studies this separation occurs naturally if the bulk solvent is presented as a continuum as in the work of Dogonadze \textit{et.al.}[4, 1] for ET and SHS[50] for PCET.

To single out the solvent reorganization energy, a solvent polarization coordinate \( Q \) is introduced. As detailed in Ref. [50] this coordinate introduces a new parametric dependence to the electron, proton, and vibrational Hamiltonians, wave functions and energies. Here it is shown how an additional solvent coordinate modifies the ET reactions and the PCET kinetics can be treated analogously.

First, a solvent coordinate \( Q \) is introduced. The solvent coordinate is orthogonal to other coordinates which allows writing the wave function as \( |imaN\rangle = |iN(q, Q)\rangle |mN(Q)\rangle |aN\rangle \) where \( |aN\rangle \) is the wave function related to solvent polarization. Similarly the energies from Eqs. 33 in the main paper obtain a parametric dependence on \( Q \). The initial state solvent wave functions are eigenfunctions obtained from
\[ [\hat{T}_Q + \epsilon_{mN}] |aN\rangle = E_{aN} |aN\rangle \]  

and similarly for the final state. Above, \( \hat{T}_Q \) is the kinetic energy operator for the outer-sphere species. Then the total energy is given by

\[ E_{imaN} = \varepsilon_{iN} + \varepsilon_{mN} + E_{aN} \]  

and the total coupling between the initial and final states is

\[ V_{imaN,fnbN} = \langle fmbN | \hat{V}_N | imaN \rangle \approx \langle fN | \hat{V}_N | iN \rangle \langle nN | mN \rangle_q \langle bN | aN \rangle_{Q} \]

Assuming that the outer-sphere free energy related to the solvent reorganization is independent of the particle number allows separating its contribution from the total grand partition function

\[ \Xi_i = \sum_{m,a,N} \exp\left[-\beta(E_{imaN} - \mu N)\right] \]

and the total coupling between the initial and final states is

\[ V_{imaN,fnbN} = \langle fmbN | \hat{V}_N | imaN \rangle \approx \langle fN | \hat{V}_N | iN \rangle \langle nN | mN \rangle_q \langle bN | aN \rangle_{Q} \]

where \( p_{imN} = \exp[-\beta(\varepsilon_{iN} + \varepsilon_{mN} - \mu N)]/\Xi_{im} \) and \( p_{aN} = \exp[-\beta EaN/Q_a] \). As done above, representing the delta function as a Fourier transform allows writing

\[ k = \sum_N \frac{V_{iN}^2}{\hbar^2} \int dt \left\{ e^{it(\varepsilon_{mN}/\hbar)} e^{-it(\varepsilon_{aN}/\hbar)} \right\}_q \times \langle e^{it(EaN/\hbar)} e^{-it(EaN/\hbar)} \rangle_{Q} \]

where auxiliary correlation functions \( G_{mn,N}(t) \) and \( g_{ab,N}(t) \) are introduced providing a connection to the work of SHS[50, 41]. To be specific, \( G_{mn,N}(t) \) characterizes the inner-sphere contributions while \( g_{ab,N}(t) \) is related to the outer-sphere solvent polarization.
Different approximations for the correlation functions presented by SHS in Ref. [50, 41] can be readily used here as well to derive various well-defined limits of the rate equation. For example, assuming that the intra-molecular modes can be neglected leads to Eq. (38) with \(a/b\) replacing the \(m/n\) indices. Within this assumption and repeating the steps leading to Eq. 31 of the main paper shows that resulting reorganization energy is the solvent reorganization energy and the inner-sphere interactions contribute only to the reaction energy.

If the intra-sphere contributions cannot be neglected, the rate equations become rather cumbersome in general. However, the case \(G_{ab,N}(t) \approx G_{ab}(t)\) i.e. that the outer-sphere contribution to rate is independent of the particle number, deserves some attention. For this, the inner- and outer-sphere components are separated by rewriting Eq. (49) using a convolution[53]

\[
k = \sum_N p_{iN} \frac{2\pi V^2_{if,N}}{\hbar} \int dEf(x)F(\Delta E^N_{fi} - x) \tag{51}
\]

with \(f(x) = \sum_{mn} p_{mN} S^2_{nm,N} \delta(\epsilon_{mN} - \epsilon_{nN} + E)\) and

\[
F(E^N_{fi} - x) = \sum_{ab} p_{aN} \mathcal{S}^2_{ab,N} \delta(E_{aN} - E_{bN} + \Delta E^N_{fi} - x)\text{ as shown for single } N\text{ in Ref.}[53].
\]

\(f(x)\) and \(F(E^N_{fi} - x)\) represent inner- and outer-sphere contributions to the activation energy. Again various forms for both terms can be derived[53]. To retain consistency, a high-temperature approximation for quadratic solvent modes is used. This gives[53, 50, 41]

\[
F(E^N_{fi} - x) = \frac{1}{\hbar \sqrt{4\pi k_B T\lambda^N_o}} \exp \left[ -\frac{(\Delta E^N_{fi} + \lambda^N_o)^2}{4k_B T\lambda^N_o} \right] \tag{52a}
\]

\[
f(x) = FC(\Delta E - x)_i \tag{52b}
\]

where \(FC(\Delta E - x)_i\) is a modified Franck-Condon factor given in \(44\) and \(\lambda^N_o\) is recognized as the outer-sphere reorganization energy. Making the high-temperature and slow-fluctuating Debye solvent approximations as done in Eq \(44\) allows performing the convolution integral. This yields \[53\]

\[
k = \sum_N p_{iN} \frac{2\pi V^2_{if,N}}{\hbar} \frac{1}{\hbar \sqrt{4\pi k_B T(\lambda^N_o + \lambda^N_i)}} \exp \left[ -\frac{(\Delta E^N_{fi} + \lambda^N_o + \lambda^N_i)^2}{4k_B T(\lambda^N_o + \lambda^N_i)} \right] \tag{53}
\]

Finally the assumption that the outer-sphere contributions do not depend on the particle number can be applied to give

\[
k = \sum_N p_{iN} \frac{2\pi V^2_{if,N}}{\hbar} \frac{1}{\hbar \sqrt{4\pi k_B T(\lambda_o + \lambda^N_i)}} \exp \left[ -\frac{(\Delta E^N_{fi} + \lambda_o + \lambda^N_i)^2}{4k_B T(\lambda_o + \lambda^N_i)} \right] \tag{54}
\]

From this form it can be seen that the total reorganization energy can be separated to a particle number independent solvent contribution \(\lambda_o\) and a reorganization energy of the inner sphere component \(\lambda^N_i\) which depends explicitly on the particle number.
11. PCET kinetics within GCE

Continuing the PCET scheme set up in the paper section 4.2., the PCET rate constant is written using the Golden Rule formulation. This gives

\[
 k_{\text{GCE-PCET}} = \frac{2\pi}{\hbar} \sum_{N,u,v,m,n} e^{-\beta(E_{i\mu N} - \mu_N)} \left| \langle Nvf | \hat{V}_N | iuN \rangle \right|^2 \delta(E_{i\mu N} - E_{f\nu nN})
\]

\[
 = \frac{2\pi}{\hbar} \sum_{N} \sum_{u,v} \sum_{m,n} p_{i\mu N} \left| \langle Nvf | \hat{V}_N | iuN \rangle \right|^2 \delta(E_{i\mu N} - E_{f\nu nN})
\] (55)

The obtained form is analogous to the GCE-ET theory developed herein and shares the structure of the canonical PCET rate of SHS. As assumed for ET part, it is expected that the vibrational part of the system does not depend on the number of particles. However, no such assumption is made for the transferring proton i.e. the proton potential depends on the charge state. This is written as

\[
 \Xi_i = \sum_{N,u,m} e^{-\beta(E_{i\mu N} - \mu_N)} \approx Q_m \sum_{N,u} e^{-\beta(\epsilon_i N + \epsilon_{iu} N - \mu_N)} = Q_m \Xi_{iu}
\] (56)

At this point it is important to stress that the vibronic coupling depends sensitively on the proton donor-acceptor distance \( R \) which is included in the rate expression. It is assumed that the coupling can be decomposed as

\[
 \langle Nvf | \hat{V}(R)_N | iuN \rangle \approx \langle Nvf | \hat{V}(R)_N | iuN \rangle_q \langle Nn|mN \rangle_Q = V(R)^N S_{nm}^N
\] (57)

Inserting these two approximations result in PCET rate constant of the form

\[
 k_{\text{GCE-PCET}} \approx \frac{2\pi}{\hbar} \sum_{N,u,v} e^{-\beta(\epsilon_i N + \epsilon_{iu} N - \mu_N)} \Xi_{iu} \sum_{m,n} e^{-\beta\epsilon_{mN}} |V(R)^N_{uv}|^2 \left| S_{mn}^N \right|^2 \delta(E_{i\mu N} - E_{f\nu nN})
\]

\[
 = \frac{2\pi}{\hbar} \sum_{N,u,v} p_{i\mu N} \sum_{m,n} V(R)^N_{uv} \left| S_{mn}^N \right|^2 \delta(E_{i\mu N} - E_{f\nu nN})
\] (58)

This form is amenable to the direct treatment as performed by SHS. Depending on the treatment of the \( R \) coordinate, several appropriate limits may be considered each yielding a different canonical rate constant. The derivations for the \( R \)-dependent PCET rates follow a similar (but more complex [41]) cumulant expansion as performed above for ET. Hence, the GCE-PCET rate can be obtained by extending the approach presented above for the ET. The extension of PCET in GCE is straightforward and here I present only the most simple result valid under the same conditions as the Marcus-like expression derived above for ET. Specifically, one assumes that i) the short time approximation of the energy gap correlation is valid, ii) high-temperature limit is taken, and iii) that the \( R \) coordinate gives Eq. 36 of the main paper.
12. References

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