

Alkali metal ion effects to hydrogen evolution on gold surface

Master's thesis

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Abstract

The hydrogen evolution is an extremely important reaction in modern electrocatalysis. It has many practical applications, such as hydrogen generation, and has been extensively investigated in the past several years. However, the atomic-scale details remain unclear for this fundamental reaction. One of the recent topics in this field is the effect of alkali metal cations on hydrogen evolution reaction on the gold and platinum electrode. Experimentally, it has been shown that, in the presence of different alkali metal ions, the activity of hydrogen evolution reaction can change notably, but the reason why this occurs is not well understood. Computational tools, such as density functional theory and powerful computers, have provided a microscope for building this kind of understanding. This thesis uses the grand canonical ensemble density functional theory as a computational tool to understand the effects of the alkali metal cation on hydrogen evolution on a gold electrode. It was shown that the cations indeed affect to thermodynamics and kinetics of the hydrogen evolution. However, in comparison to experiments, it was shown that the model used in the thesis could not explain the experiments completely, so the model needs to be more, for example, by adding dynamics, reorganization of solvent or nonadiabatic effects that were not present in the model.

Tiivistelmä

Vedyn kehitysreaktio on erityisen tärkeä modernissa elektrokatalyysissä. Sillä on paljon tärkeitä sovelluskohteita, ja sitä onkin tutkittu paljon viime vuosien aikana. Vaikka kyseessä onkin tärkeä reaktio, ei sen atomitason käyttäytymistä ole pystytty täysin ymmärtämään. Yksi viimeaikaisista tutkimuskohteita on ollut alkalimetalli-ionien vaikutukset vedyn kehitykseen kulta- ja platinaelektrodeilla. Kokeelliset havainnot ovat osoittaneet, että eri alkalimetalli-ioneilla on erillainen vaikutus vedyn kehitysreaktion aktiivisuuteen, mutta tätä ei ole täysin selitetty. Laskennalliset menetelmät kuten tiheysfunktionaaliteoria ja tehokkaat tietokoneet tarjoavat tehokkaan mikroskoopin reaktion ymmärtämiseksi. Tässä Pro Gradu -tutkielmassa hyödynnetään suurkanonista tiheysfunktionaaliteoriaa alkalimetalli-ionien vaikutusten ymmärtämiseksi vedyn kehitykseen kultaelektrodilla. Osoittautuu, että kationit todella vaikuttavat vedynkehityksen reaktioenergiaan ja aktivaatioenergiaan. Kuitenkin tutkielmassa käytetty malli ei täysin kyennyt selittämään kokeellisia havaintoja, joten mallia on parannettava esimerkiksi ottamalla huomioon dynamiikka, liuottimen uudelleenjärjestäytyminen tai ei-adiabaattiset efektit, joita malli ei sisältänyt.

Preface

This Master's thesis was performed at the University of Jyväskylä in the computational catalysis group led by Professor Karoliina Honkala during the fall of 2022 and spring of 2023. The thesis was supervised by Academy Research Fellow Marko Melander. The literature was searched from Jykdok and Google Scholar, and some was provided by the supervisor. Electrocatalysis, proton-coupled electron transfer, and hydrogen evolution were generally considered, and calculations were computed with GPAW by the CSC supercomputer Mahti.

The author thank Karoliina Honkala for the possibility of doing this project and Marko Melander for the interesting topic, excellent instructions, and all the preliminary material. I want to also thank the great teachers and lecturers for the teaching and all of my fellow students for the great five years I had when I studied chemistry at the University of Jyväskylä.

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Used abbreviations

DFT - Density functional theory

SCF - Self consistent field

GCE-DFT - Grand canonical ensemble density functional theory

LDA - Local density approximation

GGA - Generalized gradient approximation

Beef-vdW - Bayesian error estimation functional with van der Waals corrections

SJM - Solvent jellium model

BFGS - Broyden–Fletcher–Goldfarb–Shanno algorithm

NEB - Nudged elastic band

CINEB - Climbing image nudged elastic band

PCET - Proton-coupled electron transfer

ET - Electron transfer

PT - Proton transfer

HER - Hydrogen evolution reaction

RHE - Reference hydrogen electrode

1 Introduction

Catalysis is a process in which some chemical species make chemical reactions easier to occur by offering an alternative pathway for it.^{1,2} The catalysis is important for our society, for example, in modern industry and to handle climate change.^{2,3} Catalysts make reactions faster, but that is not the only criterion for a good catalyst. Its production cost, toxicity, lifespan, and easy but also versatile use are also a criterions. Often the main consideration is its fundamental purpose of making reactions faster.

One main branch of catalysis is electrocatalysis, that combines electrochemistry with catalysis. Then catalyst is always the electrode of the electrochemical cell. The electrode material is often a metal or semiconductor in the electrochemical cell. The catalyst transfers electrons from the electrode to some molecule or vice versa in the progress of catalysis. Electrocatalysis is industrially very important since, for example, the production of hydrogen through hydrogen evolution or the conversion of carbon dioxide into something useful relies on electrocatalysis but at the same time, electrocatalysis is an extremely complicated topic, which became clear later.⁴ This thesis goes under the topic of electrocatalysis, but the focus is on the particular reaction called proton-coupled electron transfer and a particularly example of it called hydrogen evolution, which plays a huge role in electrocatalysis but also has interesting behavior in experiments and simulations.

In electrocatalysis one of the important reactions are proton-coupled electron transfer reactions that have attracted the interest of scientists because of their unclear mechanism and the important role they play in catalysis. From reactions in fuel cells⁶ to many biological processes, understanding proton-coupled electron transfer is required.^{7,8} In principle the process sounds simple because, very briefly speaking, it is a simultaneous transfer of proton and electron.⁹ Electron transfers, such as reduction-oxidation reactions, and proton transfers, are quite common reactions in nature, but so are proton-coupled electron transfers. Some reactions that might seem to be only proton transfers are actually coupled with electron transfers. It is still not fully understood when all the complicated quantum mechanical details are presented. The role of the reaction conditions and reaction environment is also not well understood. The main question is how quantum-mechanically the proton needs to be described.^{6,10} These questions have been investigated experimentally and theoretically using computational methods in recent years.

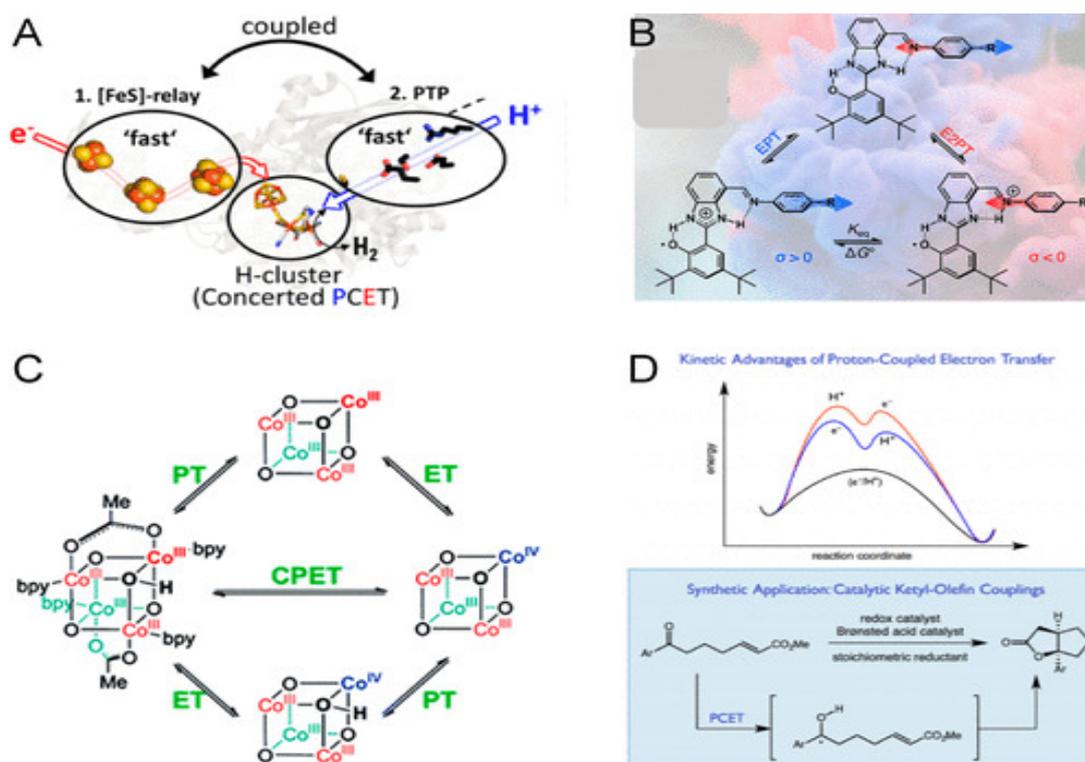


Figure 1: Examples of the proton coupled electron transfer from the different fields of chemistry. A) presents a long range PCET in hydrogenases, B) presents biomimetic PT wires, C) presents water oxidation on metal oxides and D) redox catalysis by PCET activation. Figure illustrates how diverse reactions proton-coupled electron transfers are.⁵ Reprinted with permission from <https://pubs.acs.org/doi/10.1021/jacs.0c09106> Copyright (2021) American Chemical Society.

This Master's thesis considers one of the most important proton-coupled electron transfer reactions, that is, the hydrogen evolution, and Figure 2 can show why this is a case. Figure 2 shows that hydrogen evolution serves an important purpose in society along with ammonia synthesis and carbon dioxide reduction to useful chemical. One could also see the fact that electrochemistry is the central part of all of these reactions.³ This also motivates the research done in the thesis.

Today, hydrogen evolution is being studied a lot with computational methods. Water is, of course, the proton donor, and often the gold or platinum surface is its acceptor. Later, we see that experiments¹¹ have shown that hydrogen evolution is affected by pH and the electrolyte. The thesis focuses on the latter. The computationally popular density functional theory^{12,13} was used for the computations, but the "standard" version is not enough. Electrocatalysis is performed with constant electrode potential and in the

electrolyte, so the grand canonical ensemble density functional theory and the solvent model are needed.^{14,15} These are discussed in Section 6.

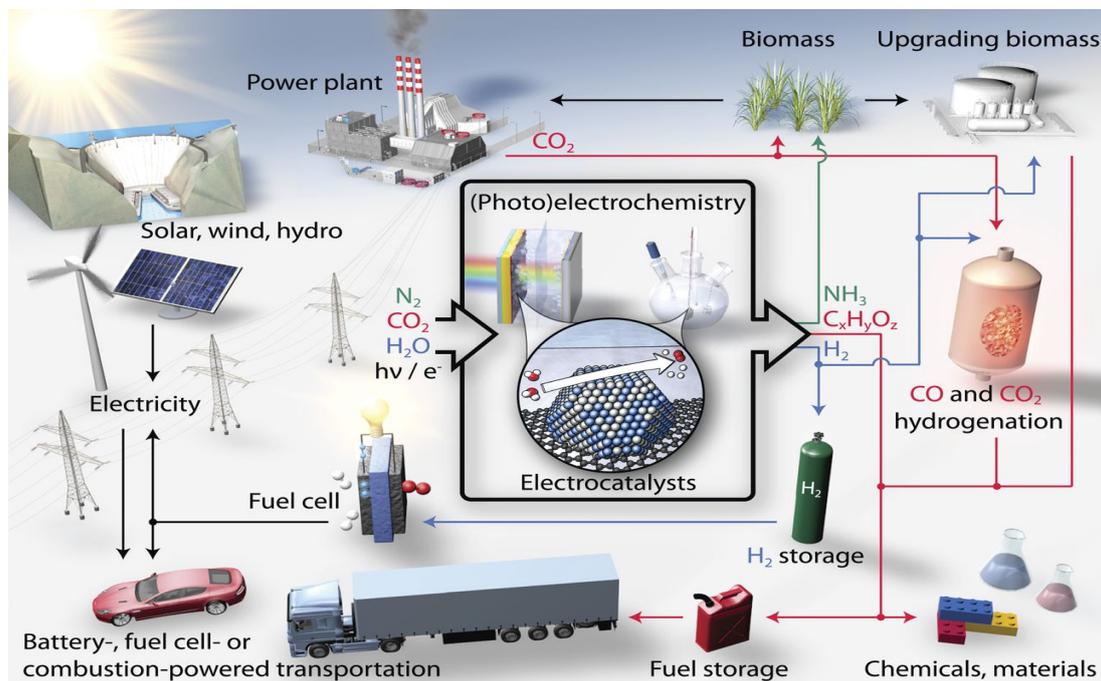


Figure 2: Hydrogen evolution central part in society along with ammonia synthesis and carbon dioxide reduction, which gives the motivation for the thesis. Electrocatalysis gives possibility do these reactions in the normal temperature and pressure using renewable energy. Ammonia is important chemical for fertilizers, Carbon monoxide can be converted to useful organic chemicals like methanol and water can be converted to hydrogen which can be used in fuel cells for instance.³ From She, Z. W., Kibsgaard, J., Dickens, C. F., Chorkendorff, I., Nørskov, J. K. and Jaramillo, T. F., Combining theory and experiment in electrocatalysis: Insights into materials design, *Science*, **2017**, 355. Reprinted with permission from AAAS.

2 Electrochemistry and electrocatalysis

2.1 Electrochemistry

Electrochemistry is a branch of chemistry that investigates the relations between voltage and chemical changes. Reactions of interest are those in which electrons move from one species to another. This means that in these types of reactions other species lose electrons, which is called oxidation, and other species receive electrons, which is called reduction. Together, the species form a redox-couple. In electrochemistry, the system is often the electrochemical cell that consists of two metal electrodes, anode and cathode, which are in contact with the electrolyte, which is an ionic solvent that conducts electricity. Oxidation occurs always at the anode, and reduction occurs at the cathode. Electrodes are connected to each other to close a circuit so that electricity can flow. If the anode and cathode are separated into different electrolytes, then they are connected with the salt bridge. Figure 3 represents the electrochemical cell that is also a galvanic cell that produces electricity, so the reaction is spontaneous. In this case, the anode is negative and the cathode is a positive electrode.¹

It is also possible that the reaction does not occur without applied voltage to give energy in the system. In this case, the cell requires an outside voltage source, and the cell is called an electrolytic cell, and the process is called electrolysis. The anode is now positive, and the cathode is a negative electrode. The cell could look the same as in Figure 3, in the textbooks the electrolysis is pictured as in Figure 4.¹

2.2 Electrochemical quantities

In the experimental electrochemistry two main quantities are current j flowing through the cell and cell potential E_{cell} , which is defined as differences in the cathode and anode potential as the following¹

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}. \quad (1)$$

Potential and current give macroscopic information about the reaction. The cell potential tells us about reaction thermodynamics and kinetics. Later in the thesis, this will be seen more concretely in the discussion of hydrogen evolution on the gold surface. The cell

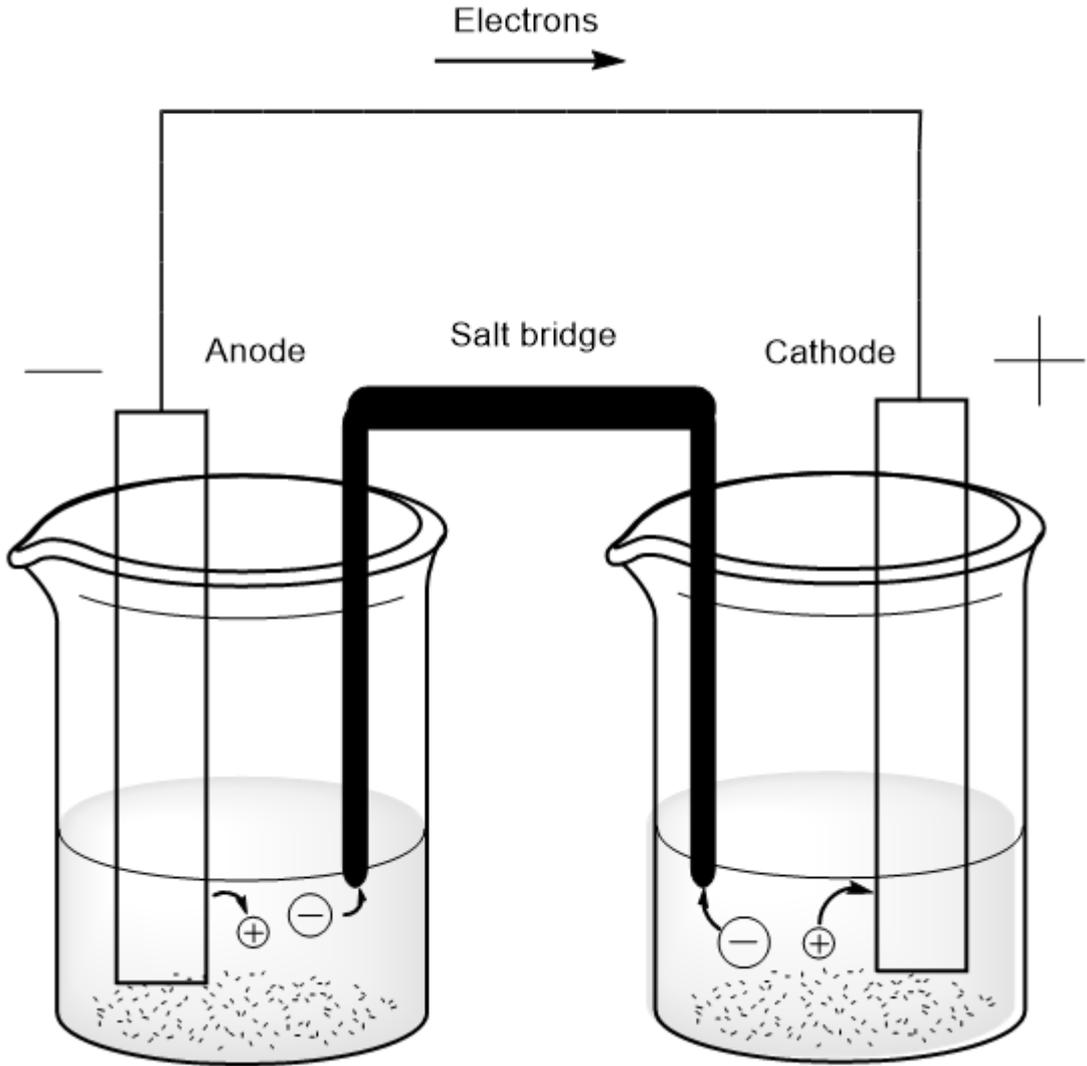


Figure 3: Example of an electrochemical cell. Electrons flow from anode to cathode which is spontaneous direction of the reaction.

potential is related to thermodynamics by the so-called Nernst equation¹

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{RT}{zF} \ln Q, \quad (2)$$

where $E_{\text{cell}}^{\ominus}$ is standard potential, which is potential at 298 K, 1 atm pressure and in 1 M solutions, R is gas constant, F is a Faraday's constant, T is a temperature, z is stoichiometric number of electrons in the reaction and Q is reaction quotient. In equilibrium Q is the equilibrium constant K and $E_{\text{cell}} = 0$.¹ Kinetics on the other hand, is related to the current i . The simplest equation for that is called the Butler-Volmer equation¹

$$i = i_0 \left(e^{-\frac{\alpha \eta F}{RT}} - e^{\frac{(1-\alpha) \eta F}{RT}} \right), \quad (3)$$

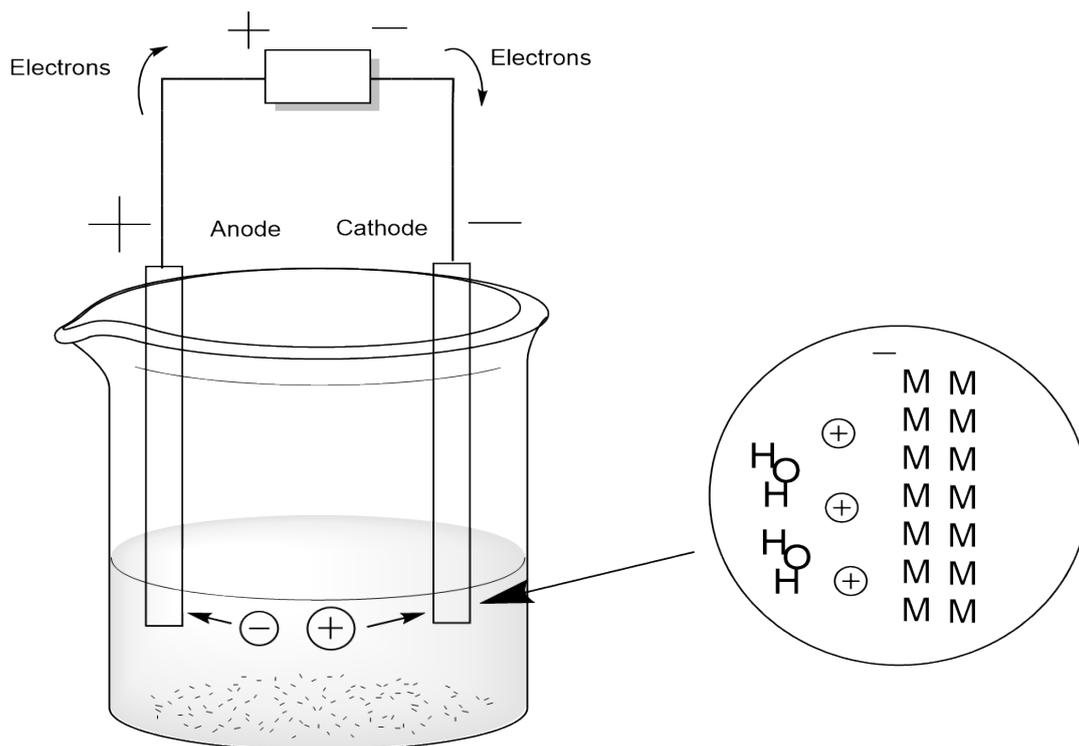


Figure 4: Electrolysis. Now electrons flow due to the applied voltage not via the reaction itself. There is also schematic picture in the microscopic structure of the electrode.

where i_0 is called the exchange current, that is, the current without net electrolysis, η is the overpotential, that is the difference between the experimental and thermodynamically determined cell potentials, and α is the symmetry factor that depends on the reaction and describes the kinetics.¹ It should be noted that the previous equations do not tell anything about the microscopic behavior of the electrochemical reaction. To obtain atomistic understanding other approaches discussed in Section 6 are needed.

2.3 Electrocatalysis

Electrochemistry combined with catalysis is a topic in electrocatalysis. For industrial and technological development this is an important topic since, as we saw in the Figure 2. However, all of the technological and industrial concerns of this topic return to atomic-scale understanding of the electrochemical components. Electrocatalysis has been extensively studied experimentally, but understanding the concept theoretically and computationally has been proven to be a difficult task. The main reason for the challenges is that these systems are complex. Things to consider are the electrode and its potential,

the interface of the electrode and liquid, pH, ion concentrations, solvent reorganization, and then all different interactions like covalent interactions, electronic interactions, dipole interactions, and solvent interactions, etc. Of course, on top of this quantum mechanics is needed to even describe chemistry of the system.^{14,16} Figure 5 illustrates the "all" complexity of electrochemical systems.

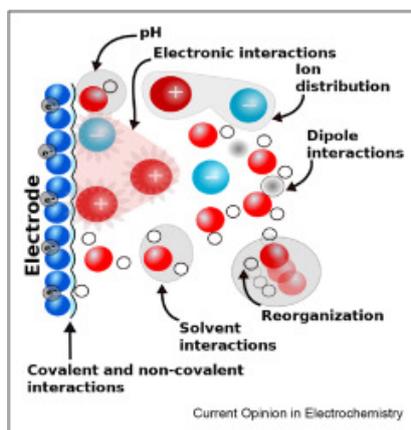


Figure 5: Electrocatalysis complexity and chemistry at electrochemical interfaces. Electrode, interface of the electrode and liquid, pH, ion concentrations, solvent reorganization, and then all different interactions like covalent interactions, electronic interactions, dipole interactions, and solvent interactions are all important in the microscopic description of the electrocatalysis.¹⁶ Reprinted with permission from authors of article: Domínguez-Flores, F. and Melander, M. M., Electrocatalytic rate constants from DFT simulations and theoretical models: Learning from each other, *Curr. Opin. Electrochemi.*, **2022**, *36*, 101110.

2.4 Electrode and electrical double layer

In an electrocatalytic cell, the electrode is often metal and reactions occur on its surface. In experiments the electrode is a macroscopic surface, but computationally the electrode is a well-defined slab. Experimentally, it is impossible to accurately know the structure and composition of the surface. There can be some distortions in the lattice, and the atoms can be packed differently, but the surface could also have some unknown configurations of adsorbates. Compared to metal electrodes, semiconductors are even more complicated because the composition of the electrode can vary.¹⁴ The most important part of the electrode, and the electrochemically the most important quantity, is the electrode potential.

This measures how favorable it is to bring the positive test charge from far away to the surface. The potential, in general, is a function of position, so it changes depending on the electrostatic environment. This is illustrated in Figure 6. Experimentally, there is always another electrode as a reference, and experimentalists measure the potential difference (voltage) between these two electrodes. Unlike experiments, computational studies have only one electrode and the scale for the potential is the so-called absolute potential, but they can be converted to each other. In principle, the electrode potential is often constant in experiments, but keeping it constant in computations is a different story, which will be explained later in Section 6.2.¹⁴

The electrode is only one component of the system, and the contents of the electrolyte cannot be neglected. In comparison to an electrode, the electrolyte is often the most complicated part of the system, since it can have a large composition of different species that are continuously moving. The local structure and composition of the electrolyte vary depending on the distance from the electrode because the electrode is charged, which implies that it can attract and repel other charged particles in the electrolyte. This forms two layers as in Figure 6 near the electrode that together form an electrical double layer. The outer layer is the so-called diffuse layer, where the potential changes exponentially and the composition of the electrolyte has approximately the same amount of positive and negative ions. The layer closer to the electrode is more interesting. The potential changes linearly, and the concentration of charged particles is higher. This layer is called the Helmholtz layer, which is even divided into inner and outer layers. The inner Helmholtz layer contains solvent molecules and adsorbed ions. The outer Helmholtz layer has ions still solvated, but they can interact with the electrode with electrostatic interactions.¹⁴

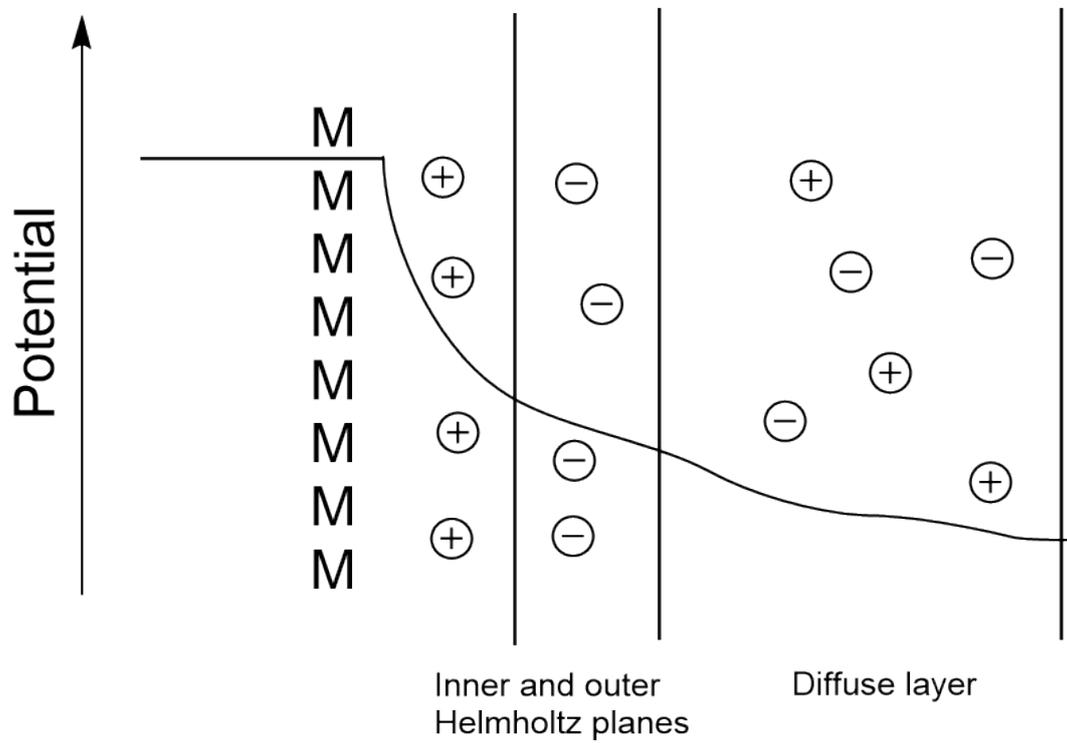


Figure 6: Electrode potential and double layer.¹⁴ Here M represents the metal electrode and pluses and minuses are ions. Inside the electrode the potential is constant but outside the electrode it decays.

3 Proton-coupled electron transfer

Proton-coupled electron transfer reactions are one of the important reactions studied in electrocatalysis. For example, hydrogen evolution, carbon dioxide reduction, and many other reactions are dependent on this type of reaction, as shown in Figure 2.^{3,6,11} The simplest proton-coupled electron transfer reaction is the situation in which the proton is transferred from some species to the surface. This thesis focuses on the transfer of a proton from water to the gold surface.

Proton-coupled electron transfer, by definition, is anything in which there is simultaneous transfer of a proton and an electron. The proton transfers from its donor to its acceptor, and so does the electron, as shown in Figure 7. The proton and electron do not need to be transferred from the same species to the same species. Donors and acceptors can be different, and proton and electron can transfer to the same direction or a different direction.⁷⁻¹⁰ In conclusion, there are a wide variety of ways that proton-coupled electron transfer can occur.

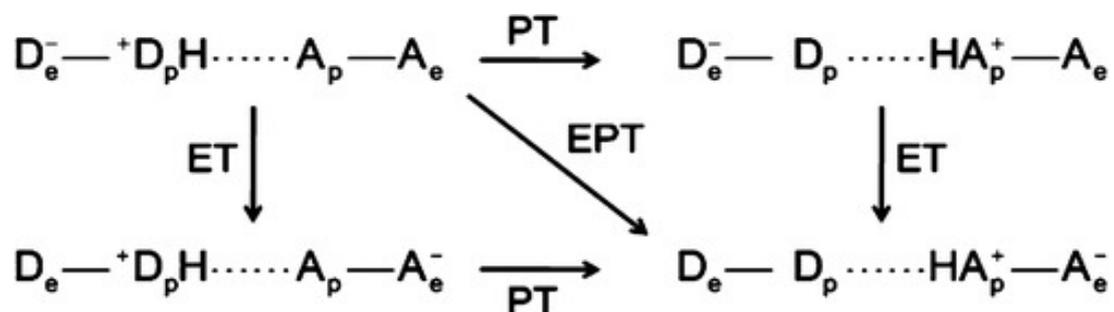


Figure 7: Mechanism. Here D and A are donor and acceptor and with subscripts e and p indicates if it is for electron or proton. Diagonal (EPT) is coupled pathway. Other reactions (PT and ET) are pathways where either proton or electron transfers first on then does the other species.⁹ Reprinted with permission from <https://pubs.acs.org/doi/10.1021/jacs.5b04087> Copyright (2015) American Chemical Society.

The easiest and most suitable way to think of proton-coupled electron transfer in an electrocatalytic reaction is to imagine an electrochemical system in which proton transfer occurs on the other electrode with the electron transfer. This is often the case in the discipline of electrocatalysis, and this is also the case in this thesis. Proton-coupled electron transfer in electrocatalysis is relevant since it occurs, for instance, in hydrogen

evolution. Of course, the proton-coupled electron transfer can also occur homogeneously, where both species are in the same phase. This is common, for instance, in enzyme reactions.^{5,7,17,18} Biological reactions are briefly described in the next section. But why are proton and electron coupled in the first place? The answer is not short since it arises from free energies and quantum mechanics.⁵ More detailed mechanistic details are considered later.

3.1 Proton-coupled electron transfer in general

This section considers a few examples of proton-coupled electron transfer reactions, in general considering mainly homogenous proton-coupled electron transfer. This illustrates that these reactions are not rare and have a role in the different disciplines of the chemistry. Although this thesis mainly considers electrocatalysis and more especially water and cation effects, which are considered in more detail in later sections, it is reasonable to note that these reactions are in the presence of other different areas of chemistry.

This thesis focuses on electrocatalytic proton-coupled electron transfer and hydrogen evolution in particular, it is important to remember that proton-coupled electron transfer also plays an extremely vital role in many biological processes. Life used these reactions a long time ago before we even understood what it was. For instance, photosynthesis, which is a crucial reaction for supporting life on Earth, goes through multiple proton-coupled electron transfer and also respiration, which keeps cells alive. Also, many other enzymatic reactions go through many proton-coupled electron transfer.¹⁹⁻²² Typical biological reaction is a situation in which smaller molecules react to form larger ones or the opposite, where the larger molecule dissociates to its parts but in any case this is catalyzed by a much larger protein molecule, which is an enzyme. For example, the energy production of cells is the cytochrome complex that catalyzes quinol oxidation and involves a proton-coupled electron transfer reaction. This reaction and its mechanism provide deep insight and understanding of proton-coupled electron transfer and its mechanism in general, since it brings nonadiabatic effects under consideration.¹⁹

Proton-coupled electron transfer is also present in organic and inorganic chemistry. Like in the biological example these reactions are also highly related to catalytic reactions, so there is a common theme. In inorganic chemistry, for instance, the water oxidation with

metal oxides has been investigated with Co_4O_4 cubane. It has been shown that there is a mechanism in which instead of consecutive electron and proton transfer there is a proton-coupled electron transfer and the mechanism depends on pH²³ Organic synthesis and proton-coupled electron transfer are often rarely considered, but considering the possibility of proton-coupled electron transfer could be crucial in understanding organic synthesis. The literature²⁴ has been considered for the catalytic cyclization reaction and the possibility of the proton-coupled electron transfer pathway, which gives the energy advantage for the reaction. The idea was to show the applicability of proton-coupled electron transfer for catalytic activation and how useful it could be in organic synthesis by considering the wide range of substrates with different catalysts.

3.2 Mechanism

In a proton-coupled electron transfer, the electron and proton transfer between their donors and acceptors. The donor and the acceptor are both local energy minimums for the electron and proton, and the transition between these two is the reaction. The proton-coupled electron transfer is often more energetically favorable path compared to the separate transfer of electron and proton, which is illustrated in Figure 8. In general, the transfer between the donor and acceptor can take place through two mechanisms. The reaction could be considered with a classical or quantum-mechanical mechanism. Because a proton-coupled electron transfer contains the transfer of two light particles, the general theory of it is based on quantum mechanical tunneling of both the electron and the proton. One main consideration is how a quantum-mechanical proton behaves.^{9,25} Electron being itself a textbook example of a quantum-mechanical particle, it is not questionable that it behaves quantum-mechanically. But a proton is 1000 times more massive than an electron, so it is possible that it does not need to be described quantum mechanically. It is still next the second lightest particle in the molecular system, so it will be next in line when adding quantum effects.

The chemical reaction is the transfer of free energy between two minimums that correspond to the reactants and the products. It is well-known that progression of the reaction can be represented as an energy diagram, where the y axis is the energy, and the x axis is the reaction coordinate, representing the progression of the reaction like in Figures 8 and 9. Different reactions use different reaction coordinates, and choice of it is not

always trivial. In the simple case, it can be bond length, for example.¹ In proton-coupled electron transfer the most logical reaction coordinate is often the proton coordinate, that is distance traveled by the proton. The energy profile describes the energy of the proton with respect to its traveled distance or solvent coordinate.^{6,9,10,26,27}

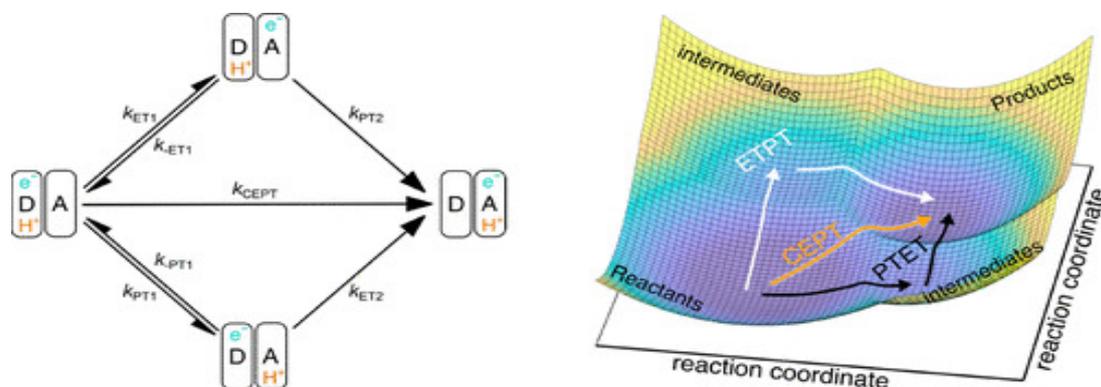


Figure 8: Proton-coupled electron transfer often provides more energetically favourable path compared to separate transfer of electron and proton.⁵ Here D and A are proton donors and acceptors and figure represents that proton-coupled electron transfer (CEPT) is energetically more favourable than separate electron and proton transfer (ET and PT). Reprinted with permission from <https://pubs.acs.org/doi/10.1021/jacs.0c09106> Copyright (2021) American Chemical Society.

As mentioned, electrons are always treated quantum mechanically in chemical reactions. If a proton is treated classically it is considered as other nuclei, meaning that electrons are considered to react instantaneously to a change in the nuclear coordinates and energy of the electronic state is a function of nuclear coordinates. This treatment is called Born-Oppenheimer approximation and in this situation, the energy surface is a smooth function of nuclear coordinates. It is usually assumed that PCET follows an adiabatic mechanism where both electrons are on the ground state. This mechanism can be obtained with quantum chemistry calculations. But the proton could behave quantum mechanically and tunnel in the reaction. This no longer gives one energy surface since the system since the proton tunnels from one quantum state to another, leading to two energy surfaces that are now two different smooth functions as shown later in the Figures 10 and 11. This mechanism is called a vibronically nonadiabatic mechanism, which is not obtained in quantum chemistry calculations in a regular way.^{6,9,10,26–29}

Electron transfer has been interpreted with Marcus theory for a long time. In Figure 9 this is represented by using harmonic free energy curves for the reactant and the product.

Nuclear coordinate includes reactants and products, but also solvents i.e. the solvent coordinate. The basic idea is that the system is distorted from equilibrium, and in the classical treatment the system fluctuates to the intersection of the energy curves, where the initial and final states have the same energy, and where electron tunneling can take place. At that point, it is possible for the electron to tunnel. Everything in addition to the electron appears to be static since electron transfer occurs on extremely small timescales.⁵

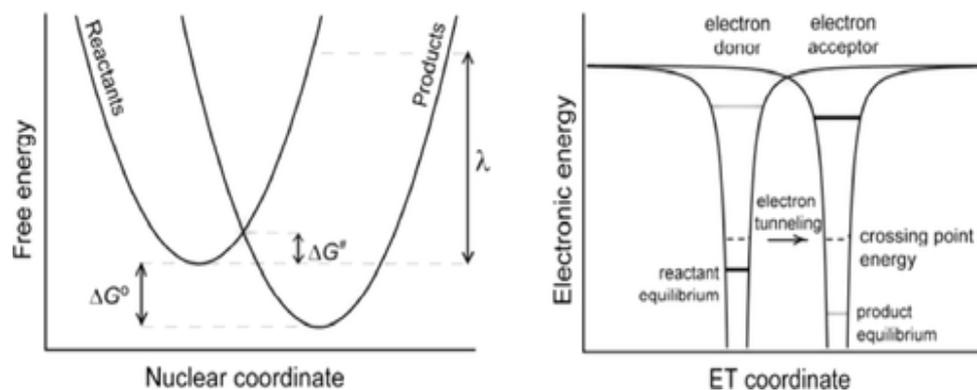


Figure 9: Mechanism of electron transfer. Reactants distort from the equilibrium and in the intersection of the energy surfaces the tunneling can occur. ΔG° is Gibbs free energy change of the reaction, ΔG^\ddagger are differences of reactants and transition state and λ is so-called solvent reorganization energy. This is in the diagram on the left. On the right at the crossing point of the the initial and final state has the same energies and electron tunneling takes a place.⁵ Reprinted with permission from <https://pubs.acs.org/doi/10.1021/jacs.0c09106> Copyright (2021) American Chemical Society

Coupling between proton transfer and electron transfer is handled by the so-called kinetic theory, which can also be considered as a generalization of the Marcus theory. In theory, the state of the system is described by a vibronic state^{10,30-32} which describes the state of the electron, the state of the proton, and the state of the rest. Division between different parts utilizes the Born-Oppenheimer approximation which uses the fact that electrons react to the movement of nuclei instantaneously, but but the Born-Oppenheimer is also extended to the movement of protons. Depending on the situation, the reaction could be electronically and vibronically adiabatic, electronically adiabatic but vibronically nonadiabatic or electronically and vibronically nonadiabatic. Electronically adiabatic means that electrons react instantaneously to change of the geometry of the system and remain on electronic ground state of the system. Vibronically adiabatic means that the proton

reacts instantaneously to motion of other nuclei and remains in its ground state. Often in this situation, the barrier for the proton transfer is small. In vibronically nonadiabatic states the situation is opposite and the barrier of the proton is high, and higher vibronic state is involved. In this situation, the proton needs to tunnel during the reaction, and its probability is proportional to the energy difference between the two vibronic states. It is also possible that the reaction is also electronically nonadiabatic. In this case electrons do not respond instantaneously to transfer of the proton, and this leads to involvement of the excited electronic state of electrons or diabatic states. The previous possibilities are illustrated in Figures 10 and 11.^{10,30-32}

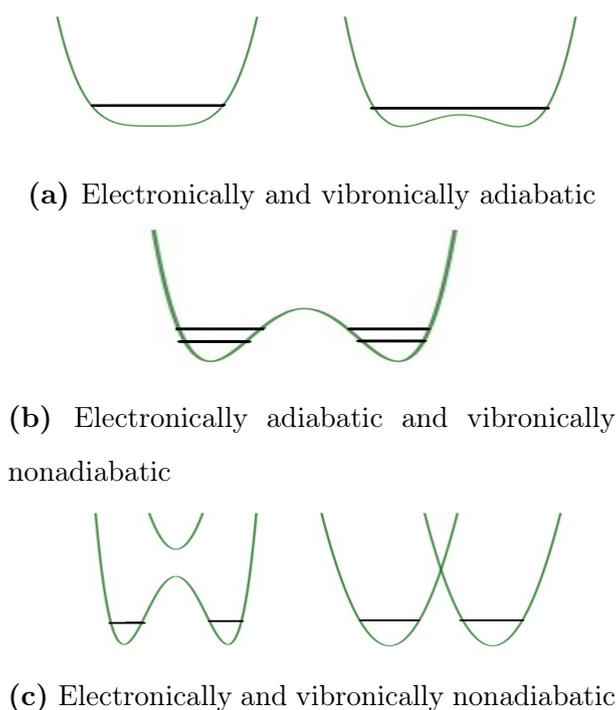


Figure 10: Electronically and vibronically adiabatic, electronically adiabatic but vibronically nonadiabatic, and electronically and vibronically nonadiabatic states. In the case (a) electrons and proton react instantaneously to change of other species and the barrier is low. In case (b), the barrier is high, and a higher vibronic state is involved, and the proton needs to tunnel in the reaction. The probability of that is related to the energy difference of vibronic states. In case (c) where electrons do not react instantaneously to the change of the nuclear coordinates so either excited vibronic (electronic+protonic) states are involved or diabatic states are required.¹⁰

A nonadiabatic mechanism of the proton-coupled electron transfer has been subject to research in the past few years, since the adiabatic mechanism cannot explain all aspects of PCET reactions such as high kinetic isotope effects. Shortly speaking, a nonadiabatic

mechanism can occur if the electronic or vibronic coupling between the two states is small, i.e. when the two states interact weakly, which means that they have the same energy in some nuclear coordinate. If the system has enough energy, it can reach this point and change state. This is allowed quantum mechanically but it should be noted that it can happen at the inter ro point because it does not violate the conservation of energy. More precisely the coupling between the vibronic states is small meaning that also the excited vibronic states need to be considered like in the Figure 11.^{6,9,10,26-29}

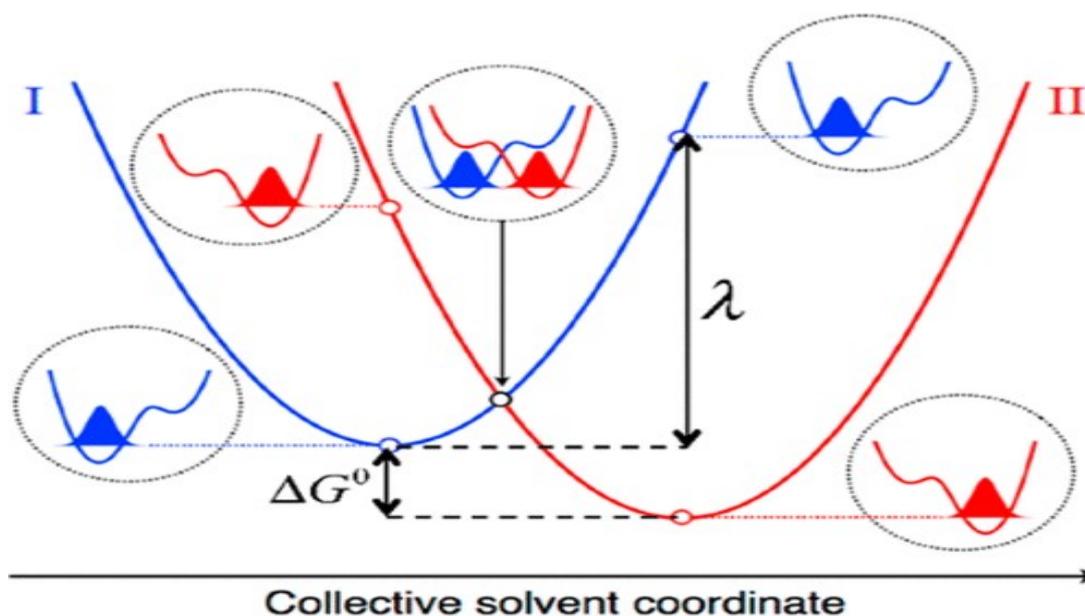


Figure 11: Vibronic states, where blue curve is for reactants and red for products. The insets present the protonic energy surfaces and corresponding proton wave functions. At the crossing point, the energy of the protonic states are equal and proton tunnelling can take place. The solvent coordinate is the collective movement of the solvent, which is now the reaction coordinate. Then there is a change in the free energy and λ is the solvent reorganization energy⁹ Reprinted with permission from <https://pubs.acs.org/doi/10.1021/jacs.5b04087> Copyright (2015) American Chemical Society.

From the nonadiabatic proton-coupled electron transfer theory it is possible to derive the following equation for the rate constant of proton-coupled electron transfer⁵

$$k = \sum_u P_u \sum_v \frac{|V_{uv}|^2}{\hbar} \sqrt{\frac{\pi}{(k_b T \lambda)}} \exp \left[-\frac{(\Delta G_{uv} + \lambda_{uv})^2}{4k_b T \lambda_{uv}} \right], \quad (4)$$

where u and v are states of the donor and acceptor, P_u is probability distribution of states, V_{uv} is coupling term which describes adiabaticity, h is the Planck's constant, λ is

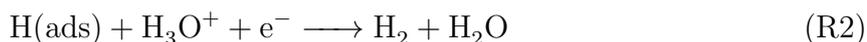
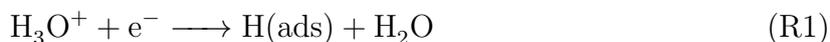
reorganisation energy, that describes the role of the solvent and double layer, and ΔG_{uv}^o is the change in the free energy, which is related to electrode potential according to the Nernst equation in electrocatalytic reaction so potential also controls the kinetics of the proton-coupled electron transfer in electrocatalysis. It could also be mentioned that the coupling term is related to the so-called tunnel splitting which is previously mentioned energy difference, and is related to the tunneling probability⁵ This is something that was considered in my Bachelor thesis.³³

3.3 Proton-coupled electron transfer in electrocatalysis

Even though electrocatalysis is a well-studied topic, it is still a very challenging field of study for proton-coupled electron transfer to understand it with atomistic simulations. Electrocatalysis itself means that we have an electrochemical system, so we have some sort of electrode, which is often metal, and the reaction takes place at the electrode-electrolyte interface, and both electrode and electrolyte control the reaction. Figure 12 shows examples of how proton-coupled electron transfer could occur in electrocatalysis. There are many things that affect the nature of the reaction, for instance, its thermodynamics and kinetics as we remember from the Nernst equation and Butler-Volmer equation (equations 2 and 3). Certainly, the solvent and electrode used have an effect, but some quantities such as electrode potential, temperature, and pH also have their own effects, as suggested by experimental evidence.^{14,15,29} This section focuses on a particular example of the proton-coupled electron transfer reaction in electrocatalysis.

One of the most important proton-coupled electron transfers in electrocatalysis is the hydrogen evolution reaction, which converts water to hydrogen as shown in Figure 2. The reaction has been extensively investigated in recent years for its importance, but also for the reason that this simple reaction is not well understood.

The reaction mechanism of the hydrogen evolution depends on the pH. In acidic conditions, it is the following^{11,35}



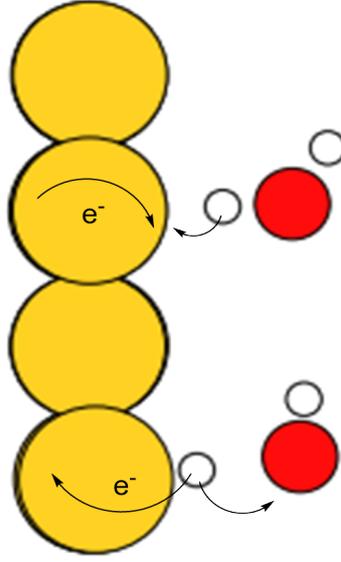
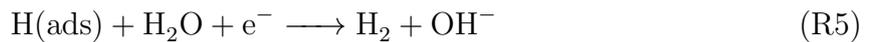
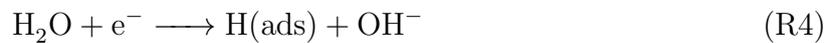


Figure 12: Mechanisms of proton-coupled electron transfer in electrocatalysis . Top reaction involves the case where electron comes from the electrode and proton from molecule. Bottom reaction electron leaves to electrode and proton leaves the surface.³⁴ Note that top one as an example is the Volmer step of the hydrogen evolution and bottom one is the inverse of it.



and in alkaline conditions it is¹¹



The first step of the reaction, that is, reactions R1 and R4, is called the Volmer step, the second step, that is, reactions R2 and R5, is the Heyrovsky step and the last and common step is called the Tafel step.^{11,35} Our interest is the Volmer step in alkaline conditions, that

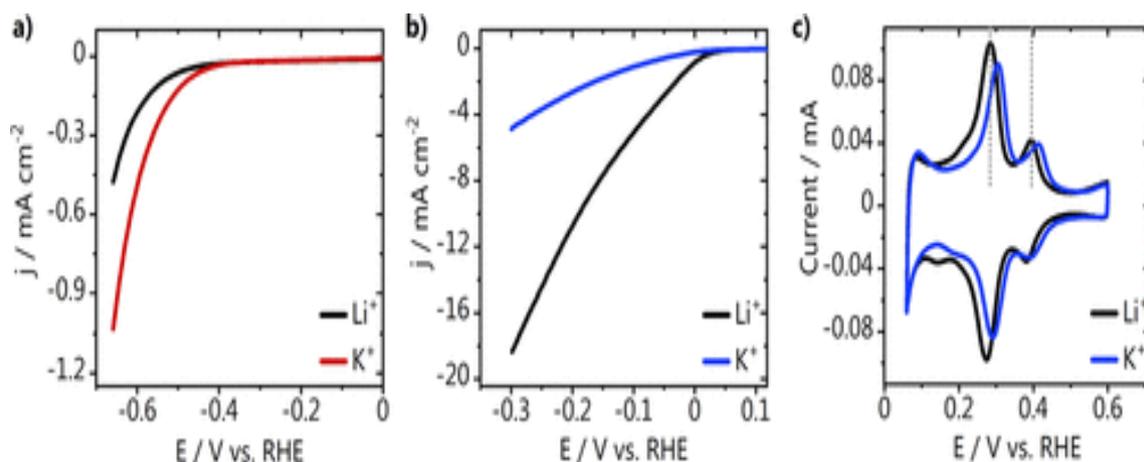


Figure 13: Effect of electrode and electrolyte to the hydrogen evolution. The electrode is gold in a) and platinum in b) and c). Figures a) and b) tells that platinum is better catalyst overall since the current increases more compared to gold in the smaller potential scales. For the gold in the presence of the potassium ion activity is higher compared if there is lithium ion. On the other hand situation is flipped in the case of platinum. Currently it is unknown why the ion effects to the activity of the hydrogen evolution.¹¹ Reproduced from Monteiro, M. C., Goyal, A., Moerland, P., and Koper, M. T., Understanding Cation Trends for Hydrogen Evolution on Platinum and Gold Electrodes in Alkaline Media, *ACS Catal.*, **2021**, *11*, 14328–14335. Copyright © 2021 The Authors. Published by the American Chemical Society <https://pubs.acs.org/doi/10.1021/acscatal.1c04268> under the Creative Commons Attribution license <https://creativecommons.org/licenses/by-nc-nd/4.0/legalcode>.

is, reaction R4 and how the different different alkali metal ions effect the thermodynamics and kinetics of that step. It is also the rate-limiting step of the reaction.^{11,35}

Experimentally¹¹ considering the quantities such as electrode potential and current as in Section 2.2 it has been revealed that different alkali-metal ions and pH affect the activity of the reaction. Figure 13 shows how the current with respect to the applied voltage differs with the lithium and potassium ion and on the gold and platinum electrodes. Also Figure 13 shows that the platinum is better catalyst for the reaction since current currents are larger in the same potential range. It is not well understood why the alkali metal ions make a difference, and this will be considered later in the thesis with the gold electrode. It can be seen that potassium increases activity and the thesis attempts to explain why this is a case.

In Figure 14 the effect of pH to hydrogen evolution is presented experimentally. Changing the pH to more acidic does not change the order of the different ions, but changes the activity since the different reaction mechanisms compete. The effects of the pH are not considered in the thesis, but are worth at least mention. Figure 14 also shows that the ion trend changes in the more reductive potentials. This is probably because larger cations start to block the reaction by accumulating on the surface.¹¹

The main question about hydrogen evolution is: What determines its activity and why? This is not an easy question to answer, since Figures 13 and 14 state that the electrode, ions and pH have their own effect. These are also experimental observations that are not well explained theoretically and computationally. The rest of the thesis continues with hydrogen evolution and focus is to understand it more deeply. The effects of the alkali metal ions play a central role and the aim of the thesis is to explain their behavior.

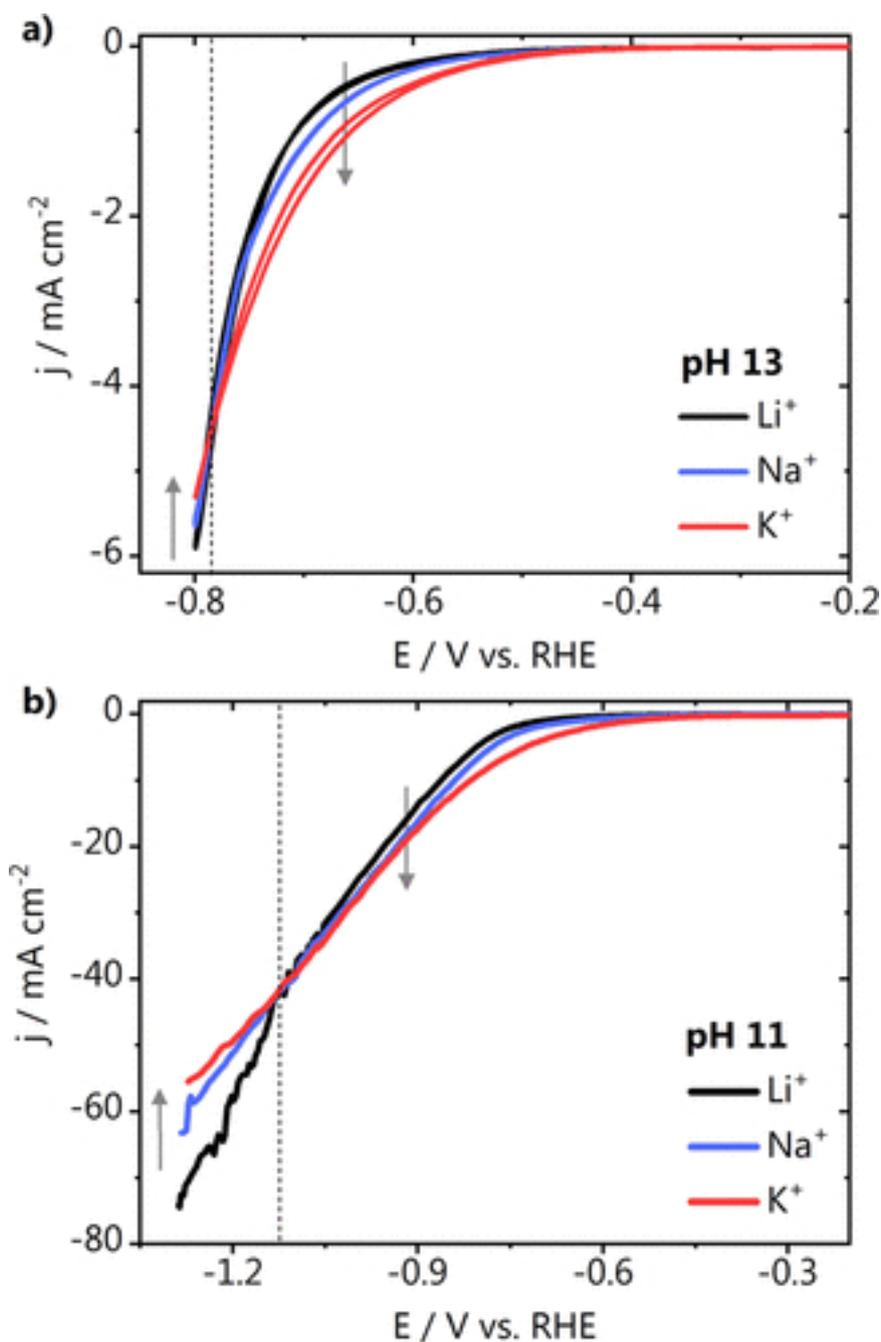


Figure 14: Effect of pH to the hydrogen evolution on the gold electrode. In the lower pH activity increases overall regardless of the ion since it opens acidic pathway to reaction. Order of the ions is not changed but the interesting aspect of the figure is that order of the ions flip after some potential value. This phenomena likewise the full effect of the pH is also not fully understood in the atomic scale.¹¹ Reproduced from Monteiro, M. C., Goyal, A., Moerland, P. and Koper, M. T., Understanding Cation Trends for Hydrogen Evolution on Platinum and Gold Electrodes in Alkaline Media, *ACS Catal.*, **2021**, *11*, 14328–14335. Copyright © 2021 The Authors. Published by American Chemical Society <https://pubs.acs.org/doi/10.1021/acscatal.1c04268> under the Creative Commons Attribution licence <https://creativecommons.org/licenses/by-nc-nd/4.0/legalcode..>

4 Theory of the hydrogen evolution

As mentioned, the thesis focuses on hydrogen evolution and this section focuses it more theoretically than in Section 3.3, where it was already considered from an experimental point of view. Although it appeared that hydrogen evolution is a simple electrocatalytic reaction, it still remains unclear how and why different aspects of the proton-coupled electron transfer and double layer impact its activity. Currently there are three different theories to understand it. They are bond energy theory, double layer theory, and kinetic theory, which are discussed in detail below. Note that currently none of these theories alone can fully explain the hydrogen evolution. Of course, these theories can explain and predict certain properties of the hydrogen evolution and provide their own important aspect, but something else is needed, possibly something that combines these all.^{10,14,30,36,37}

4.1 The bond energy theory

The bond energy theory is a thermodynamic approach to explain the behavior of proton-coupled electron transfer. It basically uses the energies of the initial and final states of the transfer when considering the driving force of the reaction. The thermodynamic approach is simple and relies on simple catalytic principles. Calculations for this approach are simple and describe, for instance, the impact of electrode material in acidic hydrogen evolution quite well. However, bond theory focuses only on the electrode material and thermodynamics, which has proven to work well in acidic conditions, but not well in the basic conditions.^{30,38,39}

The bond energy theory considers only the energies and one of the fundamental principles of catalysis, called the Sabatier's principle. This principle states that, for an effective catalyst, the adsorption energy between the intermediate and catalyst surface should not be too low or high. If energy is too high, then the reaction is limited by desorption of the products. If the adsorption energy is too low, then the reaction is limited by adsorption of the reactants. If the hydrogen binding energy could explain the hydrogen evolution, one would obtain a Volcano plot that tells which material for the electrode suits best for the hydrogen evolution. In the literature these plots are common and many metals line the edge of the volcano nicely. It has been noted that in this situation the volcano disappears if, for instance, the high-adsorption energy species with oxide covering is left out. This

shows that adsorption energy of the hydrogen cannot be the only factor that determines the rate of proton-coupled electron transfer.^{30,40}

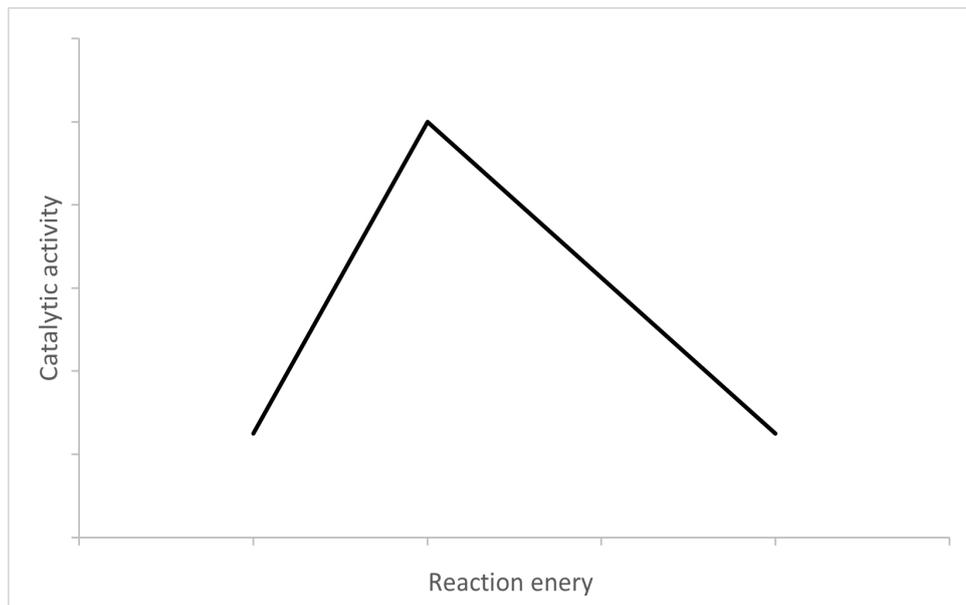


Figure 15: Volcano plot. Plot considers the reaction energy as the descriptor for the catalytic activity. If the reaction energy for a given catalyst is near the top of the volcano then it is considered to be good catalyst according to the Sabatier's principle. It is possible to obtain such a plot for the hydrogen evolution reaction. The hydrogen binding energy is used a descriptor and its energy could explain the difference between some materials. The binding energy can be either measured experimentally or computed through the density functional theory. This theory would predict that materials with the same reaction energy are equally good catalysts. One should still note that even though volcano plots can be convincing conclusions should not be done blindly from them since only thermodynamics are included.^{30,40}

4.2 The double layer theory

In general, double layer theory states that the noncovalent interactions at the electrochemical interface are important for hydrogen evolution. This covers electrostatic and van der Waals interactions between the electrode surface, reaction intermediates, solvent, and electrolyte. Unlike the bond theory, which considers thermodynamics and covalent interactions, or the kinetic theory treated below, the double layer theory attempts to capture the impact of noncovalent interactions on thermodynamics and kinetics. As such,

the double layer theory can be considered as the most complex of the three theories. Electrocatalytically the double layer theory captures many properties of the system that the bond energy theory and kinetic theory could not, for instance, take the role of the electrolyte and especially the role of the ions in the perspective of the thesis.^{37,41–44}

This theory states that in addition to the binding energy, the electrochemical interface actively modulates hydrogen evolution. Bond energy theory and kinetic theory are based on the familiar principles of thermodynamics and kinetics, but how double-layer effects, solvent, and electronic interactions should be modeled. The hydrogen evolution description of covalent and noncovalent interactions depends on the charges of the reactants, the solvent coordinate, and the distance between the reactant and the metal surface. The description of double layer theory says that the reactant comes into contact with the surface from the bulk solution, the bond between the proton and the reactant cleaves, and electron transfer makes a bond between the proton and the metal. After that, the rest of the reactant is left in the bulk solution. Figure 16 illustrates the microscopic details of the double layer theory.^{41,42}

As we recall from Section 3.3 we showed experimental results showing electrolyte, pH and potential effects on activity of hydrogen evolution. These are all quantities relevant to double layer theory. Under acidic conditions, a deprotonating ion on the catalyst surface could be a hydrogen ion, and the forming species could be water. Therefore, changing the pH could completely change a mechanism, as we recall from Section 3.3. In alkaline conditions, the Volmer step of the reaction forms the hydroxide, which is not as preferable to forming water under acidic conditions, because hydroxide has negative charge. Because the electrode is also negative, this means that the hydroxide prefers to remain in the bulk solution. Electrolytes, especially alkali metal ions, aid in that. In the presence of the alkali metal ion, the hydroxide can bond to that electrostatically because of their opposite charges. The other way to see this is that solvation decreases the electrostatic free energy of the hydroxide, so that the alkali metal makes the reaction thermodynamically more favorable. It is also possible that alkali metal ions make the transition state more stable by interaction with it electrostatically. This is why the alkali metal ion could also affect the kinetics of the reaction. The electrode potential, on the other hand, is one that decides the charge of the electrode. A more negative electrode

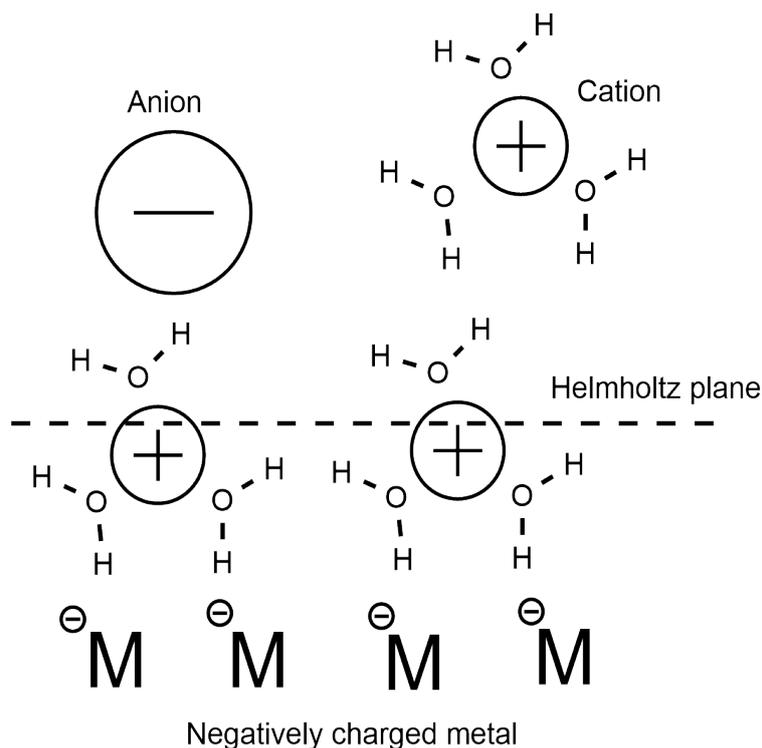


Figure 16: Double layer in the hydrogen evolution. According to the double layer theory electrolyte, pH, electrostatic interactions and potential effects all to activity of hydrogen evolution. Covalent and noncovalent interactions depends on the charges of the reactants, the solvent coordinate, and the distance between the reactant and the surface. Reactant comes into contact with the surface from the bulk solution and proton transfer to surface such that in the same time electron transfer makes a bond between the proton and the surface. After that, the rest of the reactant is left in the bulk solution.^{41,42}

means that it attracts more cations, which can interact with the hydroxide and transition state.^{35,41-43}

4.3 The kinetic theory

Last of the three theories is actually something that has been already considered, in general, for proton-coupled electron transfer in Section 3.2. It is kinetic theory. Like in the general picture of the proton coupled electron transfer, the description can use adiabatic or nonadiabatic description. In this theory, hydrogen evolution is not an exception by any means, since kinetic description of the proton-coupled electron transfer is general, so everything from Section 3.2 applies.^{10,32}

The main question in the perspective of hydrogen evolution is when the reaction needs a nonadiabatic or quantum description. It seems to be the case that in the acidic conditions adiabatic description is enough so nonadiabatic quantum effects are small. On the other hand, the alkaline hydrogen evolution cannot always be explained with the adiabatic description, so a nonadiabatic description might be needed.³² However, the description of nonadiabatic effects with the density functional theory is currently very difficult, and methods are only just being developed. Hence, this thesis assumes that the water splitting can be treated without taking nonadiabaticity or nuclear tunneling into account. All in all, proton-coupled electron transfer and, in particular, hydrogen evolution cannot be understood without kinetics, so the kinetic theory is competitive compared to bond energy theory and double layer theory, which does not consider kinetics.^{15,27,32}

5 Alkaline hydrogen evolution on gold electrode

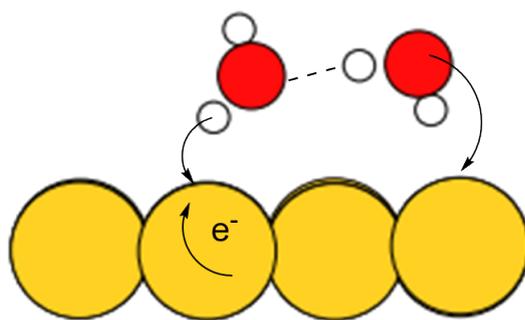
As discussed previously, the alkaline hydrogen evolution activity in gold depends sensitively on the electrolyte cation. The main goal of this thesis is to understand these ion effects, and hence this section discusses the details of alkaline hydrogen evolution on gold. This discussion is needed to establish the general trends of hydrogen evolution on the gold electrode, but also to build a realistic computational model of this reaction to investigate the cation effects.^{11,32,45}

It is not obvious how the system will behave. One claim³² is that the reaction could happen with only water under alkaline conditions. Through using a general kinetic theoretical treatment, it was proposed that in pure water the reaction proceeds through a vibronically non-adiabatic mechanism. The effects of cations such as alkali metal ions have been studied. Different cations have been studied to have different behaviors as in the Figure 13^{11,45} depending on concentration and alkalinity.⁴⁵ Cations provide quite different reaction pathways compared to only water, but since water hydrates the cations, it can change the activity-proton coupled electron transfer.

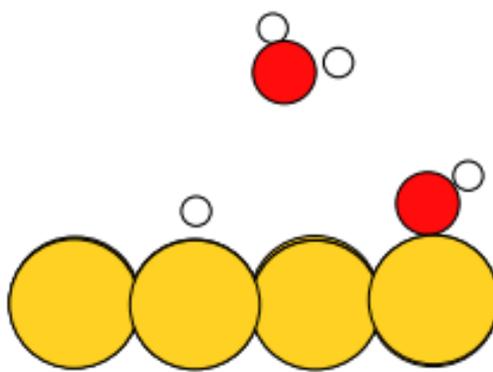
5.1 Reaction without ions

The simplest model of the electrochemical interfaces consists of just the electrode and a few water molecules. Water splitting in this simplified picture has been studied in the literature³². The issue with this model is what happens to the formed hydroxide. This probably requires that another water molecule donates a proton to the formation of hydroxide and then leaves adsorbed on the surface as hydroxide, but also in the literature³² it seems that this follows a non-adiabatic mechanism. In this way, water moves to the interface, and hydroxide is left to the surface, which could be a possible mechanism. Figure 17 shows how it shows an atomic interpretation of the mechanism.

Reference [32] provides the starting point for the thesis to start with computational methods with only water on the surface. Theoretical formulation is given in the article and it uses the diabatic formulation for the mechanism. Their goal was to improve the theoretical formulation of proton-coupled electron transfer, and with their formulation, they managed to get Butler-Volmer transfer coefficients that agree with the experiments. The



(a) Initial state



(b) Final state

Figure 17: Mechanism of the hydrogen evolution without ions. One water molecule acts as a proton donor and surface is its acceptor. Same time other proton transfer occurs from other water to original and forming hydroxide gets adsorbed to surface.

transition coefficient is related to the probability of proton tunneling, which measures the probability of the reaction. In the literature³² it is shown that the two-water model is too simple and produces high reaction energies and barriers, so that the alkaline hydrogen evolution would not take place at room temperature.

5.2 Ion effects

Ions can modulate reaction thermodynamics and kinetics through multiple effects. First, the ions control the structure and electrostatic properties of the electrochemical double layer, but importantly, they can interact with the hydroxide ion. The idea is that the ion forms a complex with water molecules and that one of the water molecules transfers a

proton on the surface, leaving the hydroxide bonded to the cation. Section 3.3 presented experimental evidence that alkali metal ions, such as lithium Li^+ or potassium K^+ , make the reaction more active. The model for the mechanism is illustrated in Figures 18 and 19 and later we see how this actually affects thermodynamics and kinetics.^{11,45}

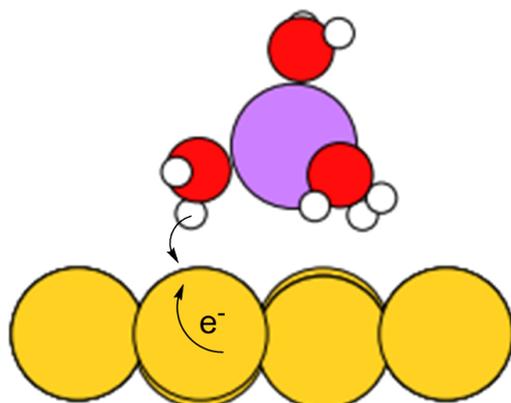
Reference [37] gives quite a wide background work on how proton-coupled electron transfer behaves with different alkali metal cations in gold but also in some other metals. The electrolyte considered was alkaline. Reference [37] also discusses the experimental influence of alkali metals to show that ion makes a difference in proton transfer activity. The trend is that activity increases from lithium to cesium, so it seems that the size of the ions has a large impact on the reaction. Intuitively, small lithium compared to large cesium should make a difference since size affects how strongly the ion hydrates.

Section 3.3 already presented some experimental results from the literature¹¹ in Figures 13 and 14 where cation trends have been investigated in hydrogen evolution with gold and also platinum electrodes. The results for lithium Li^+ potassium K^+ have already been presented there with the effects of sodium Na^+ with pH, but the article¹¹ also has a discussion of cesium Cs^+ which highlights that cesium is beneficial for hydrogen evolution on gold. Experiments conducted in the article show that lithium promotes the proton-coupled electron transfer but, for instance, potassium promotes it until concentration is too high. It was claimed that this agrees with the theoretical calculations with the same type of mechanism as in Figures 18 and 19.

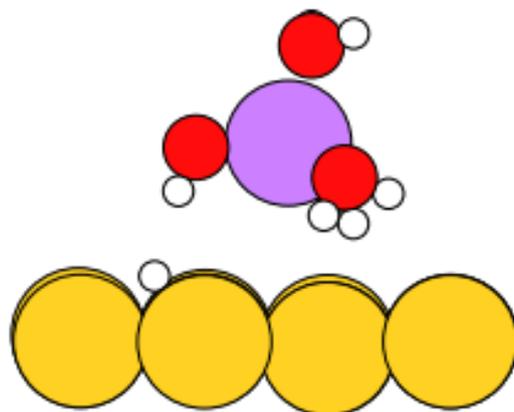
5.3 pH effects

In Figure 14 we have already seen how pH affects hydrogen evolution. Effects of pH are not the main consideration of the thesis, but, as a recap from Section 4.2 the pH mainly decides how much competition there is between acidic and alkaline hydrogen evolution. At lower pH, there are more hydronium ions that can actually be the donor of the proton. This is said to increase the kinetics of the reaction. However, the role of pH is also currently unclear.^{32,43}

Acidic hydrogen evolution has one issue when considering catalysts. Many catalysts such as less noble metals cannot be used in the lower pH by dissociation of the catalyst. This is the reason why alkaline hydrogen is often considered and the pH is typically around 13.



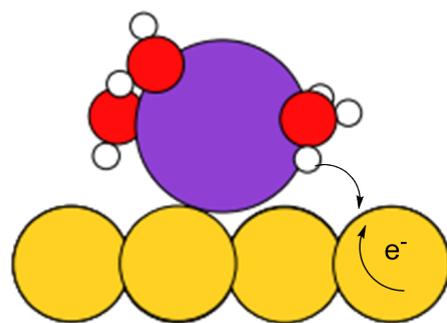
(a) Initial state



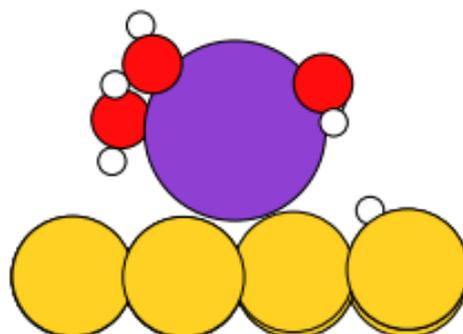
(b) Final state

Figure 18: Possible mechanism for hydrogen evolution with lithium ion. Notably, lithium stays in the solution phase and does not adsorb on the surface. One water coordinated to lithium ion acts as a proton donor and surface is its acceptor. Forming hydroxide is coordinated to lithium ion so it will be more stable than free hydroxide according to double layer theory.

It is confirmed that local alkalinity determines the concentration of ions at the electrode and weakly hydrated ions fasten the reaction, but competition of two mechanisms from Section 3.3 can hinder the reaction. Also, at lower pH, a more reducing potential is required to reach a given current to reach local alkalinity.^{32,43} Overall the pH 13 will be our interest and its effects will not be considered further.



(a) Initial state



(b) Final state

Figure 19: Possible mechanism for hydrogen evolution with potassium ion. Notably, the potassium ion adsorbs on the surface, unlike the lithium ion. Hypothesis is the same as in the case of lithium. One water coordinated to potassium ion acts as a proton donor and surface is its acceptor. Double layer theory states that the hydroxide coordinated to potassium will be more stable than free hydroxide.

6 Modeling of proton-coupled electron transfer of water on gold surface

6.1 Density functional theory

Density functional theory is a quantum mechanical method that, unlike typical quantum chemistry methods, does not use the wave function but describes the state of the system using only the electronic density. It is reasonable to give some idea what it is all about, but let us first review the basics. In quantum mechanics, Schrödinger's equation and the wave function that comes from its solutions contain all the information of the system. Almost always in chemical problems the first step is to use the Born-Oppenheimer approximation, which uses the fact that the nuclei are much heavier than electrons to separate the Schrödinger's equation in the two problems that are one for the electrons and one for the nuclei. The electronic part is parameterized with nuclear coordinates and it is assumed that the nuclei move with an average potential of the electrons when solving their positions^{46,47} Born-Oppenheimer is often useful, but the kinetic theory of Section 4.3 provides examples where it breaks down, so it could also be a limitation here. Computational chemistry uses different methods that often try to solve approximately this problem, as it is actually unsolvable analytically.⁴⁷

There are a lot of methods to try to make progress towards the solution but for quantum chemistry density functional theory is probably the most popular. Other methods try to find an approximate wavefunction but density functional theory proves that it is enough to find the electron density which is a function of one 3D coordinate instead of the wavefunction which is a function of the coordinates of $3N$ electrons. This makes density functional theory an efficient approach. The proof that the electron density can exactly describe the ground state of electrons is based on the Hohenberg-Kohn theorems. The first theorem basically states that the energy of the system is a unique functional of the density, where a functional is a function that maps the density to the number via the integral. The second theorem states that ground state density minimizes the energy functional. These theorems are the foundation of density functional theory. In figure 20 theorems provide connection between density and the system.^{12,13,46,48}

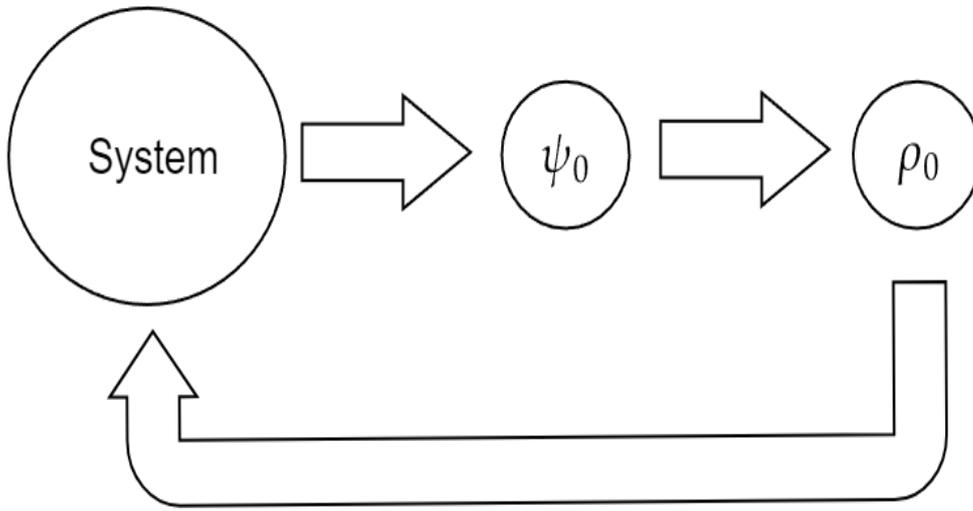


Figure 20: In quantum mechanics system, more precisely, its hamiltonian determines the ground state wavefunction of the system and all properties can be computed from it. This includes the ground state electron density. Hohenberg-Kohn theorems states that the ground state density actually determines also the system so it is enough to find the density which is the function of three coordinates instead of wavefunction that is a function of $3N$ electrons. This makes density more feasible to handle than wavefunction.^{12,13,46,48}

However, these theorems do not yet provide a practical way to solve the electronic structure problem. Kohn-Sham method is the first step in progress towards the solution. Kohn-Sham introduces an auxiliary, non-interacting electron density which allows presenting the many-body quantum problem exactly using a single-electron formalism in practice; this introduces the single-electron orbitals which are required to reproduce the true density of the interacting system. Like before, this makes initial guess for electron density from which functional could be calculated and Kohn-Sham system can be solved. From the solution the new electron density is obtained, and this is repeated until the density matches closely enough to the previous density. The ground state could be determined from the final density. This is illustrated in Figure 21.^{12,13,46,48}

Although the density functional theory is exact, there is still one problem. Problem is that exact form of the functional that includes non-classical interactions, which is called

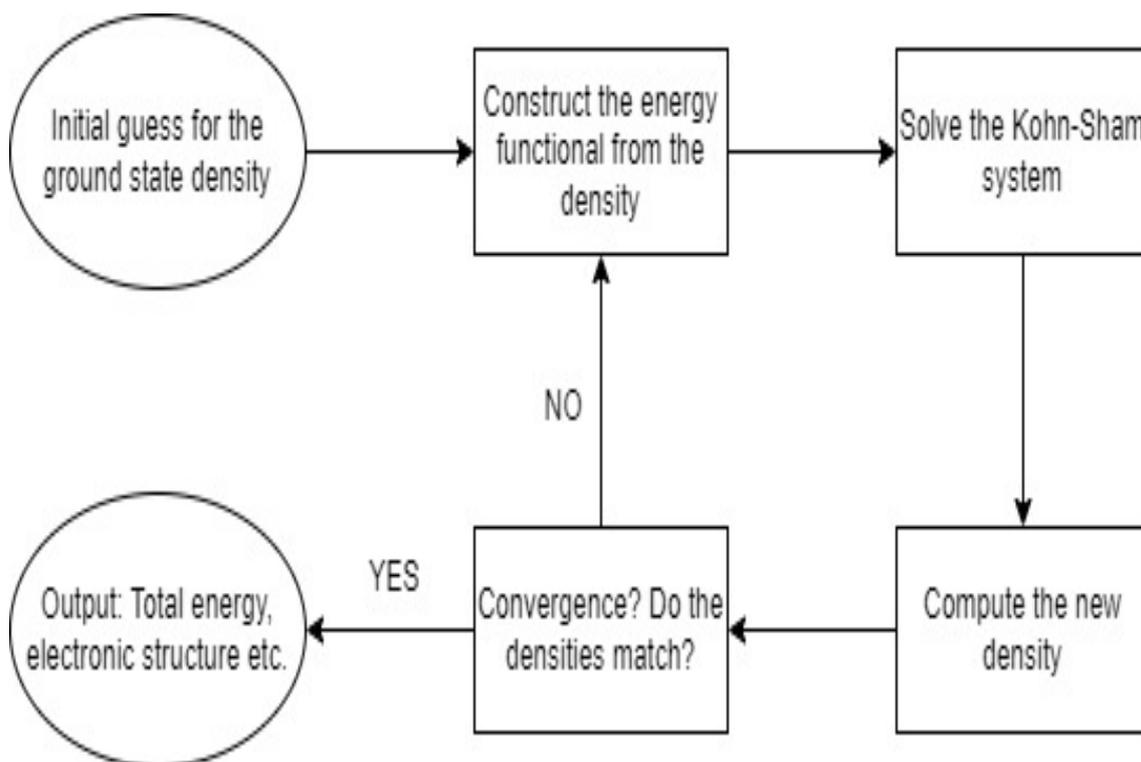


Figure 21: Practical density functional theory calculations begin by guessing the ground state electron density. With that one can construct the energy functional and then solve the Kohn-Sham system to get the new density. If this density matches the guess then calculation is converged and relevant quantities can be computed from the density. If not then from the new density new energy functional can be constructed and cycle can be repeated until the convergence is achieved. Cycle is called self consistent field (SCF) cycle.^{12,13,46,48}

an exchange-correlation functional, is not known. Mathematically, it has packed in all expressions for which we do not have analytical expressions. This functional can still be approximated with different levels of accuracy. The exchange-correlation functional can be constructed through either only theoretical arguments or using data fitted to experiments.⁴⁶ The most simple functional in use is the LDA functional, which assumes basically that the density does not vary much.^{46,49} Of course this is not usually a good functional, so something better such as GGA functional, which also includes the gradient of the density, is used.^{46,50} Anyway there are a lot of functionals available and the choice of the functional is probably the most crucial step when performing the calculations. This work uses Becke-vdW functional because it should be able to capture with reasonable accuracy all the relevant interactions like the van der Waals interactions.⁵¹

In this project the density functional theory is used with a little modification to track how much electrons move in the system, reaction energies but most importantly the thermodynamics and barriers. The reaction thermodynamics is obtained from the energies of the initial and final-state energies. The reaction barriers have been computed using the NEB method, which produces a discretized potential energy surface. In practice, NEB joins the initial and final states together with images connected by artificial springs. The springs and images form a band that is optimized by calculating the forces in the band. The transition state will be the snapshot with the highest energy. Quick note in the end the nudged elastic band of then gives to low energy for transition state, so with modified version called climbing image nudged elastic band which basically tries to "climb" the transition state to larger energies will be used to get more realistic results.⁵²

6.2 Grand canonical density functional theory

The standard density functional theory discussed in the previous section uses the fixed number of electrons in the system. However, electrochemical experiments do not fix the number of electrons or charge of the electrode, but rather the electrode potential. To model of constant electrode potential conditions, one needs to use the grand canonical density functional theory approach, which allows the number of electrons to change and by that keep electrode potential constant. The thesis also uses this since the system under the interest is electrochemical. The difference is that standard density functional theory uses internal energy to describe a system, but grand canonical density functional theory uses the grand potential of the system. This allows the number of electrons to vary, which is now crucial for making sure that the potential does not change. As a thermodynamical term, a grand canonical ensemble is used to quickly point out that the particle number is allowed to vary around its expectation value. More technical details can be found in the literature. Briefly speaking, one can go from internal energy to grand potential by the Legendre transform. Figure 22 illustrates the idea of the grand canonical density functional theory.^{14,15}

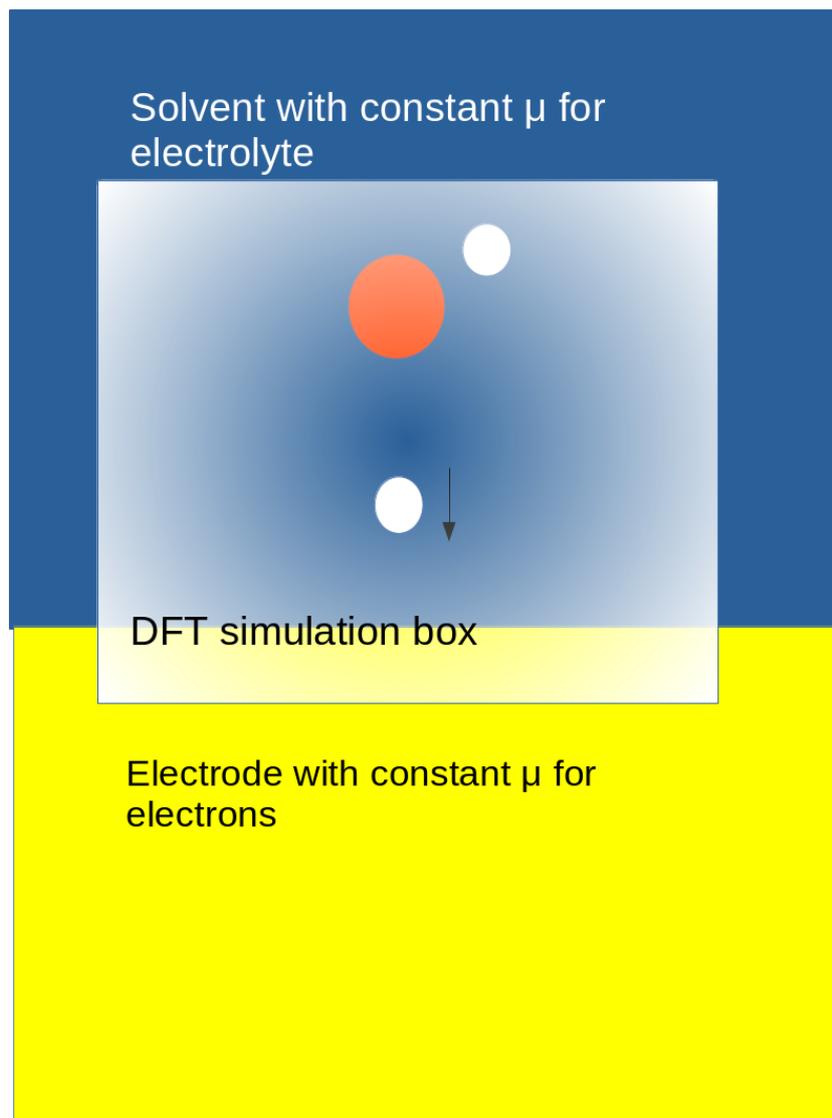
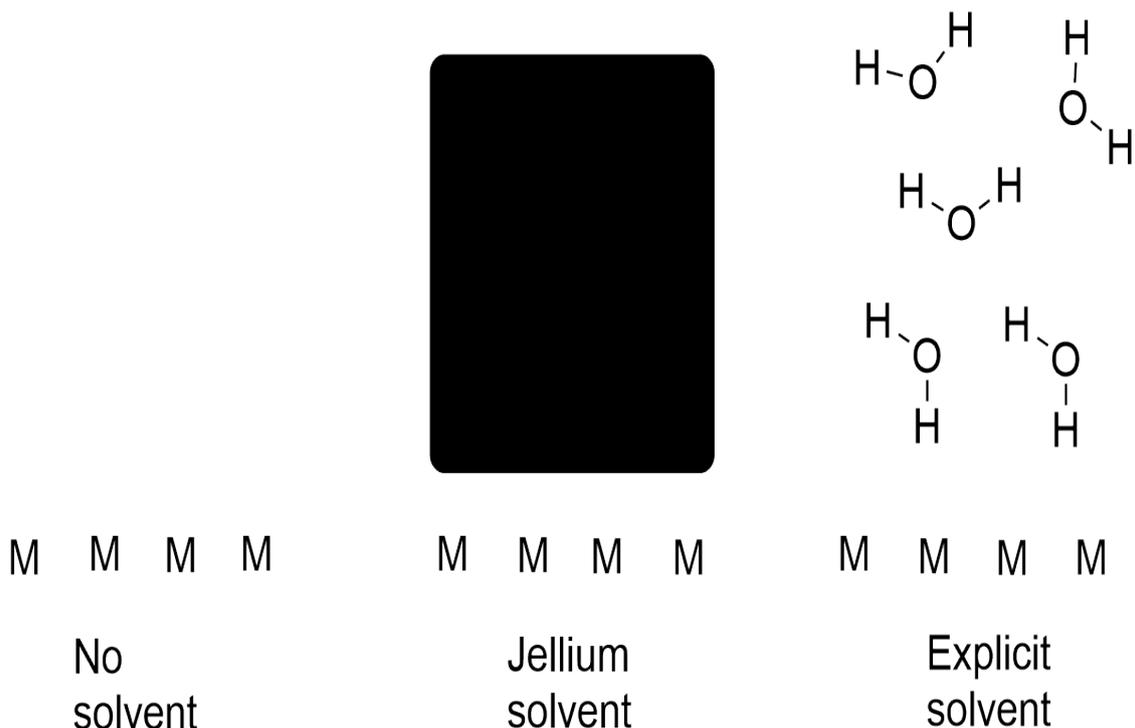


Figure 22: Grand canonical density functional theory considers solvent as source of the electrolyte and electrode as the source of the electrons with both having constant chemical potential μ . Thermodynamically density functional theory considers energy, but grand canonical ensemble uses grand potential, which is one of the many thermodynamic potentials and it fits best in the system where particle number is allowed to vary. In actual simulations we can consider that the system is in density functional theory the simulation box and we can change a number of electrons in it. Simulation finds the optimal average number of electrons as an expectation value.^{14,15}

6.3 Solvent model

Like previously stated the electrocatalysis takes place at a solid-liquid interface, see Figure 5. Standard density functional theory is done in vacuum, so in addition to the grand canonical ensemble density functional theory, the solvent model will be necessary. The solvent is always present in an electrochemical system and is often water. Solvent in the real world consists of large amounts of water molecules and electrolyte ions around the system of interest so there can be a lot of explicitly defined molecules. The problem is that it would make the calculations extremely heavy. A computationally more feasible alternative is the use of a dielectric continuum model, which considers the solvent as a linear dielectric. Let us quickly review this. Between the metal and the solvent, there is an empty space, called a cavity, where reactions occur, which is defined by the cavity distribution function. The solvent itself is described with Poisson equations with linear dielectric function or permittivity. It is often also necessary especially with water to add some terms to take van der Waals interactions into account. Technical details can be found from the literature^{14,53}. With solvent and grand canonical ensemble density functional theory we can describe an electrochemical system. This can be represented visually with Figure 23.

This thesis uses a combined implicit-explicit solvent model in which only the most important water molecules close to the ion and interfaces are treated explicitly, while the majority of the solvent is described through the continuum model. This way, one can include the most important ion-water-metal interactions and still have a computationally feasible presentation of the system. In practice the representative structures are taken from ab initio molecular dynamics simulations⁴⁵ and look like the ones in Figures 18 and 19.



used as a calculator and the potential was controlled by changing the number of excess electrons. Geometry optimization was carried out using the BFGS method⁵⁵ with a maximum force of 0,05 eV/Å. Kohn-Sham equations were solved with the grid spacing used in the calculations being 0.18.⁵⁵ NEB and CINEB⁵² calculations were performed with 10 images with 0,10 eV/Å convergence criterion. All scripts are in the Appendix.

6.5 Assumption, merits, and limitations of the computational model

The model for the hydrogen evolution used in this thesis used to describe the hydrogen evolution has a lot of details and is fairly complicated. This model can already give answers to many questions about hydrogen evolution. First, the model yields the reaction energies, so the bond energy theory could be used to answer how the ions affect thermodynamics. This model also has electrode, potential, and electrolyte, so it has aspects of the double-layer theory, but the problem is that the electrode-electrolyte interface is static, so solvent reorganization and dynamics are not considered. It is highly possible that the behavior of the electrolyte is more dynamic than expected. Finally, from the NEB-plots the activation energies and hence kinetics are obtained, so the kinetic theory is also applicable but is also limited. This is because the reaction is considered adiabatically, so nonadiabatic effects are not considered. Of course, there are also assumptions about the structures of the initial and final states, and there is also the possibility that the reaction occurs microscopically in a different way. The main question is this model enough to describe the hydrogen evolution and can it explain the experiments?

7 Results

This work aims to provide understanding of how different alkaline metal cations modulate the alkaline HER activity of the gold electrode. First, the reaction without an alkali metal ion was considered, and then with the cesium ion. Being problematic, the attention was focused more toward reactions with lithium and potassium ions. This is also why the NEB calculations were conducted only for these species. All species were calculated at 0 V and lithium and potassium also at -0.5 V. Since the reaction was alkaline hydrogen evolution the pH was 13 in all calculations and its effects were not considered. In addition, we have already presented the experimental data to compare in Figure 13. All potentials are with respect to the reference hydrogen electrode.

The Volmer step of alkaline hydrogen evolution was studied in the presence of water, cesium, lithium, and potassium to investigate how the ion impacts reaction thermodynamics and kinetics. The calculations were designed to take into account all aspects of the hydrogen evolution theories discussed in Section 4 but with the limitations discussed in Section 6.5. The water and ion structures were chosen as presentative structures of previous density functional theory data⁵⁶ and ab initio molecular dynamics⁴⁵ data.

7.1 Water

As discussed in Section 5.1, the simplest model for the electrochemical interface is one where only water is present. The model considered is presented in Figure 17. The idea in the calculations was that another water molecule not only deprotonates but also obtains another proton from the second water molecule. In figure 24 there are structures for initial and final states that were computed from different initial configurations. In Table 1 there are reaction energy and the number of excess electrons of the initial and final states. The change in the number of excess electrons at least proves that the reaction is a proton-coupled electron transfer. It can be seen that the reaction energy is quite high, which shows that this mechanism is not thermodynamically favorable. The results obtained are completely different from those in the literature³² which used a similar configuration and those results gave kinetics that could explain the experiments. However, our results show that this would not be thermodynamically favorable and that the initial and final states are not achievable within our model. Overall, it was concluded that neglecting the cations

and using only water molecules does not provide a good description of the electrochemical interface for alkaline hydrogen evolution.³²

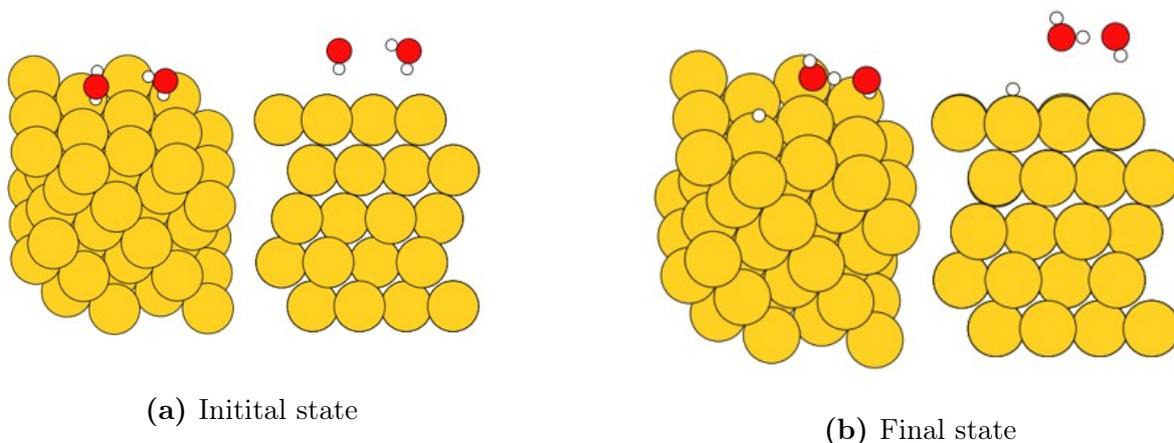


Figure 24: Optimized structures without ions. Without ions the reaction was not thermodynamically favourable so water was not considered further

7.2 Cesium

After the water cesium was the next point of interest since it was at the opposite ends of the alkali metals. It could have been an interesting ion to consider more carefully in the simulations, but it was challenging to find optimal initial and final states, because of the large size of the cesium ion, which gives a lot of room for water molecules to move around. The mechanism was considered the same as potassium in Figure 19. Cesium could float above the surface or lay on the surface, and some water molecule deprotonates to it and ion stabilizes the forming hydroxide. In Figure 25 are computed structures and in Table 1 are reaction energies which are a bit lower than with water, so in the presence of Cs the reaction is thermodynamically more favorable. Number of excess electrons again notes that this reaction is the proton-coupled electron transfer reaction. Overall, it turned out that a proper computational model for cesium could not be identified as the reaction energies show a wide spread depending on the chosen water configuration around the cesium. Therefore, cesium was not studied further and only limited conclusions can be drawn. This could already suggest that the role of the solvent is dynamic.

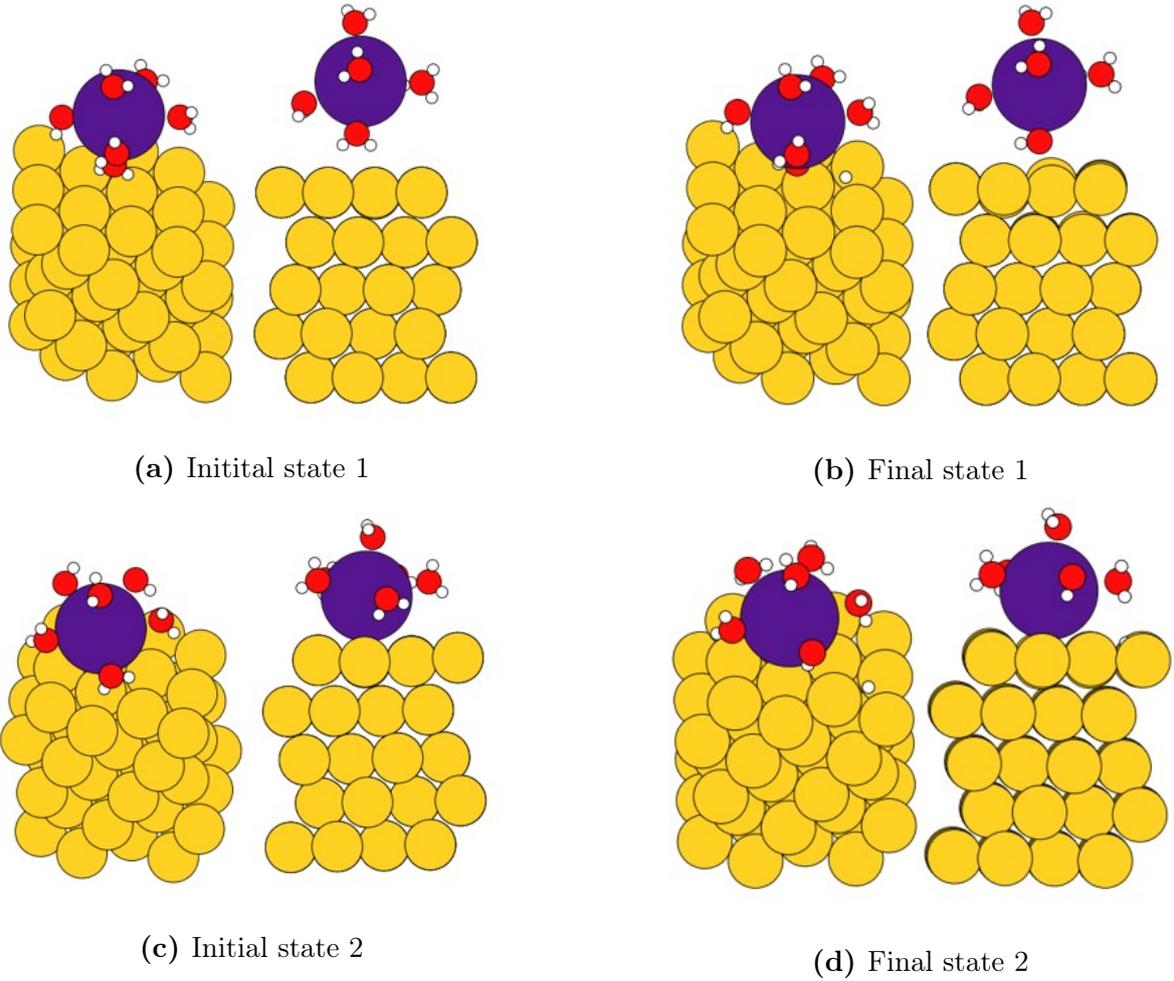


Figure 25: Optimized structures with cesium. For the purposes of the thesis it was hard to find optimal initial and final state so focus turned more towards the lithium and potassium ion. Cesium can either stay in the liquid (a and b) or adsorb on the surface (c and d)

Table 1: The computed reaction energy, change in the number of electrons, for the Volmer step on Au(111) without ions and in the presence of Ce^+ .

	Reaction energy (eV)	Change in the number of excess electrons
water	2.17	1.83
cesium 1	0.18	1.41
cesium 2	0.90	0.26

7.3 Lithium

7.3.1 Structures and NEB and in 0 V

Two different lithium water configurations were considered and these structures are shown in Figure 26. In one configuration, its tetrahedral structure breaks into a planar structure during the reaction. It was also tested whether lithium ions could lay on the top of the surface, as potassium and cesium did, but this was shown by the computations to be an unfavorable structure, since the computations converged to either of the previous ones. This was also suspected before the calculations, but was tested to prove this. The reaction energies and the number of excess electrons are given in Table 2. The reaction energy shows that this is again more thermodynamically favorable than with only water, so cation indeed has an effect on the reaction. However, the cesium structures had lower reaction energy, so it looks like cesium stabilizes the forming hydroxide more than lithium, but it depends on the configuration of the cesium. The numbers of excess electrons are similar in the cases of lithium and cesium, but significantly greater than in the case of water.

For the lithium structures, NEB calculations were carried out to find the activation energy of the reaction. Activation energies are also given in the Table 2. The energy and excess electrons are plotted against the distance of the proton and oxygen from which it is moved, since it is the most logical reaction coordinate of the system. Figure 28 provides a representative energy diagram for the first lithium structure, since other structures had a similar energy diagram. Barriers at 0 V are relatively high, being around 1.1 eV.

7.3.2 Structures and NEB and in -0.5 V

Next the same optimized structures were optimized in the -0.5 V potential to see the effect of the potential on the thermodynamics and kinetics of the reaction. These structures are shown in Figure 27. Geometrically structures are similar to those in Figure 26. On the other hand, the potential affects thermodynamics. The calculated reaction energies are shown in Table 2. There is also a change in the number of excess electrons for monitoring purposes as previously. The result shows that for the structure 1 reaction becomes thermodynamically more favorable, since the value gets lower by 0.56 eV, but for the second structure there is not much change.

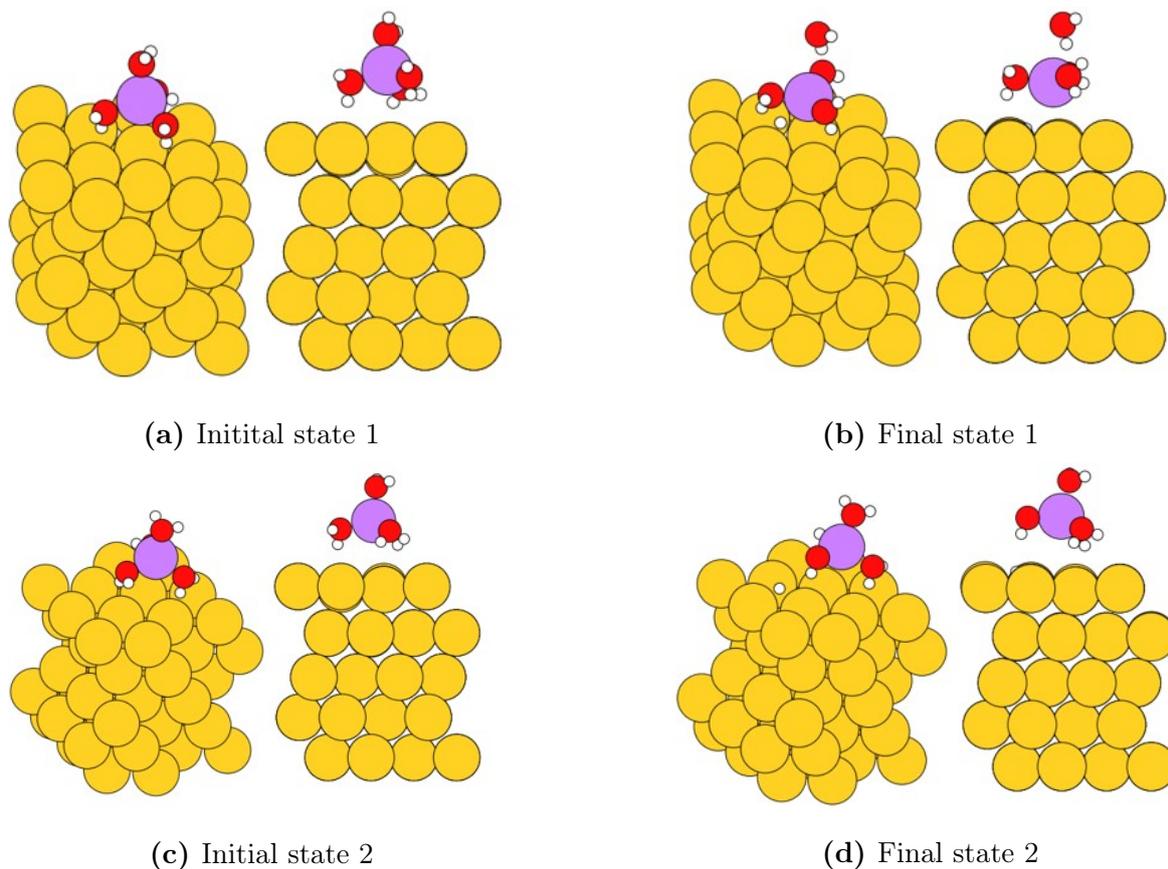


Figure 26: Optimized structures with lithium. Potential is 0 V versus reference hydrogen electrode. Essentially two different structures were obtained. One with the planar final state (structure 1) one with the tetrahedral final state (structure 2). Note that lithium is always in the liquid phase

NEB calculations were also performed to find the activation energy of the reaction in the potential -0.5 V. From the calculated activation energies in Table 2 we can also see that the activation energy has decreased as potential has been decreased. The energy and the number of excess electrons are plotted as previously in the Figure 28. The change in activation energy and is supported by the literature^{11,43,45}, and we would expect the reaction to be more exothermic at more reductive potentials to occur more likely with more reductive potentials.

Since hydrogen may cover the electrode at the considered electrode potential of -0.5V⁵⁷, it could effect in the course of the reaction. This was also tested by adding adsorbed hydrogen to structure 1 which is also shown in Figure 27 and it was proven unnecessary to include the adsorbed hydrogen. The reaction energy increased by a little by 0.10 eV and the activation energy does not significantly depend on the presence of an additional hydrogen on the surface as seen in the Table 2.

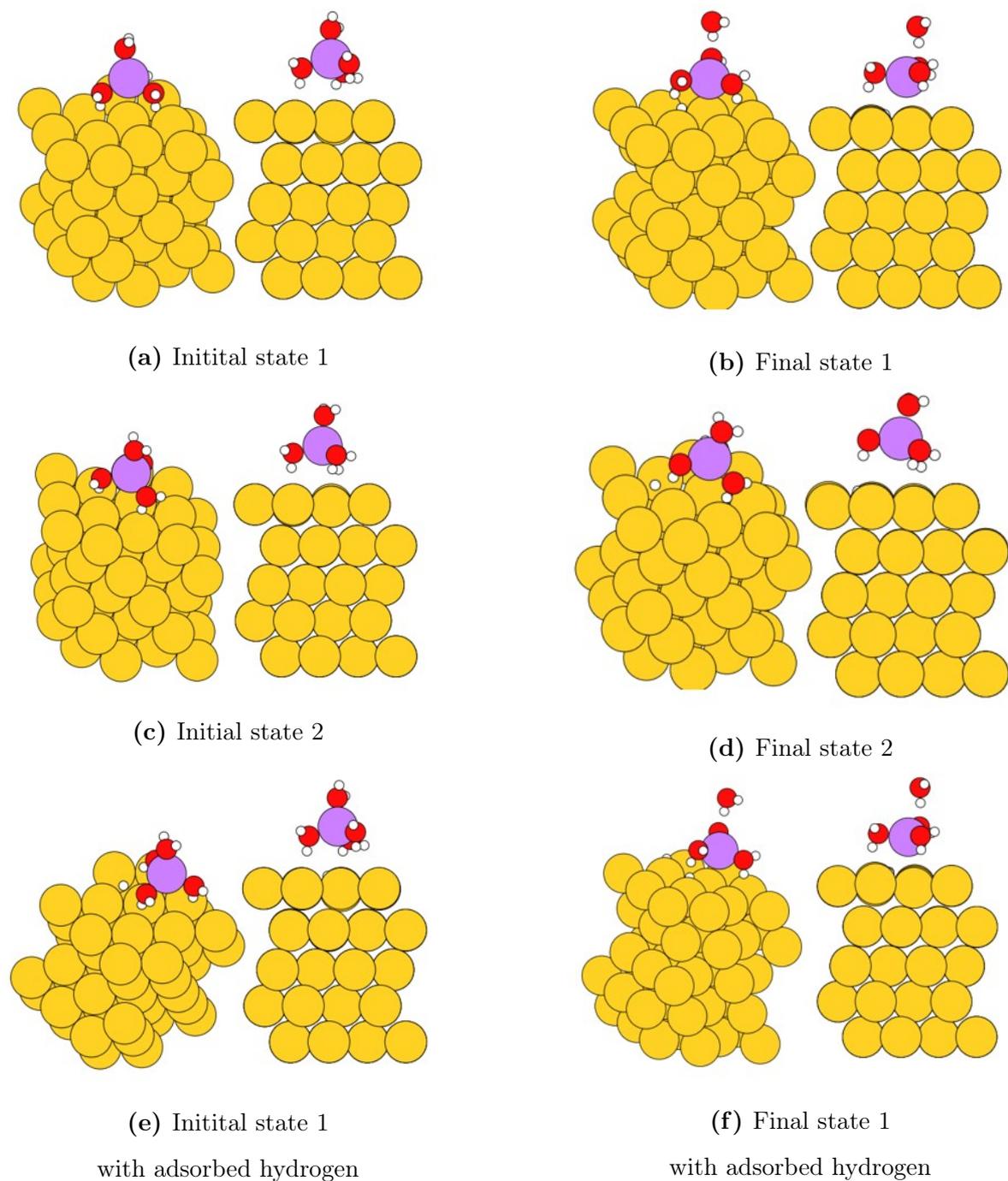
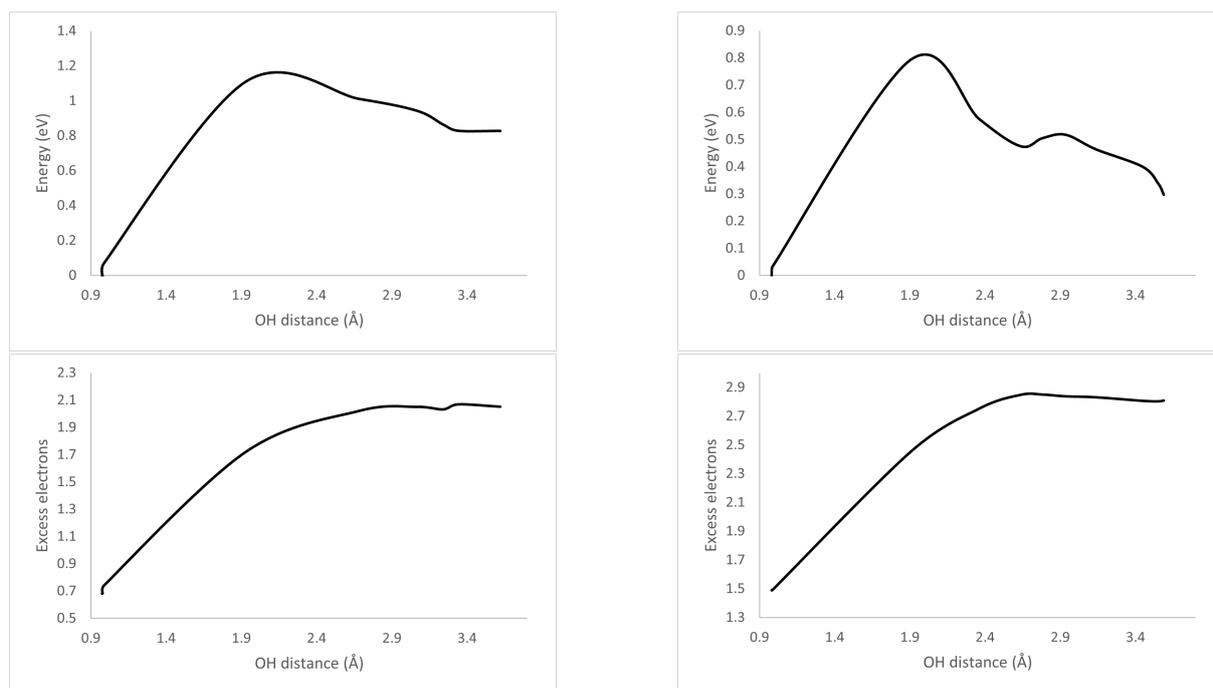
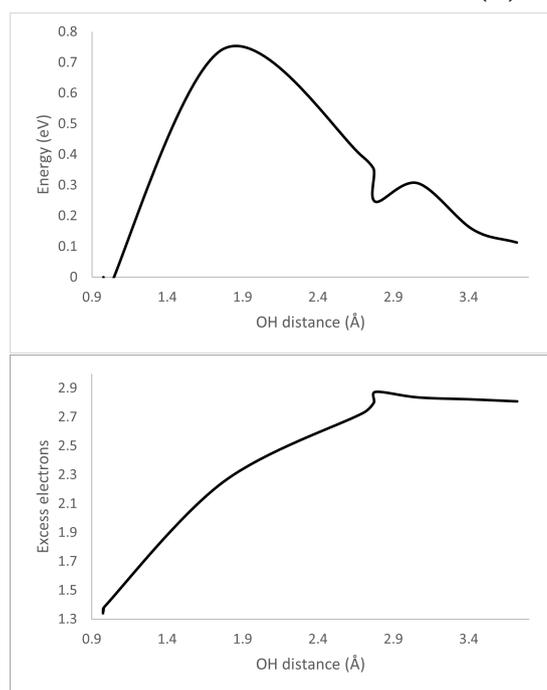


Figure 27: Optimized structures with lithium. The potential is -0.5 V versus the reference hydrogen electrode. Same structures as previous were considered. Also, the possibility of adsorbed hydrogen was considered, but it was proven that it is unnecessary according to thermodynamics and kinetics.



(a) lithium 1 at 0 V

(b) lithium 2 at -0.5 V



(c) lithium 1 at -0.5 V

with adsorbed hydrogen

Figure 28: Representative energy diagrams and evolutions of excess electron for lithium. Activation energies were obtained from these as a difference of energies of initial and transition state. Change in the number of excess electrons were monitored to see it increases smoothly to from value of initial state to value of final state.

Table 2: The computed reaction energy, change in the number of electrons, and activation energies as a function of the electrode potential for the Volmer step on Au(111) in the presence of Li^+ .

	Reaction energy (eV)	Change in the number of excess electrons	Activation energy (eV)
lithium 1 at 0 V	0.83	1.41	1.11
lithium 2 at 0 V	0.77	1.39	1.08
lithium 1 at -0.5 V	0.27	1.44	0.79
lithium 2 at -0.5 V	0.83	1.28	0.79
lithium 1 at -0.5 V with adsorbed hydrogen	0.37	1.46	0.74

7.4 Potassium

7.4.1 Structures and NEB and in 0 V

The potassium structures in the potential of 0 V are shown in Figure 29. They are like those with the cesium, which refers to the fact that in the other potassium is adsorbed to surface and on the other it floats near the surface. The reaction energies and the number of excess electrons for the potassium structures are given in Table 3. Again, as one could already expect, this is more thermodynamically favorable than only, but it looks at least for the structure 2 the reaction energy 1.12 eV is higher than energies of lithium, so overall it seems that the reaction with potassium is thermodynamically less favorable. The changes in the number of excess electrons are similar to those of lithium and cesium, so approximately the same amount of electrons move in each reaction.

For potassium, NEB calculations were carried out to find the activation energy of the reaction. Activation energies are in Table 3. The energy and excess electrons are plotted again against the distance of the proton and oxygen from which it is moved. In the Figure 31 the first potassium structure is chosen to be representative for the plot. Barriers at 0 V are relatively high, being 1.12 eV and even 1.42 eV for the other structure.

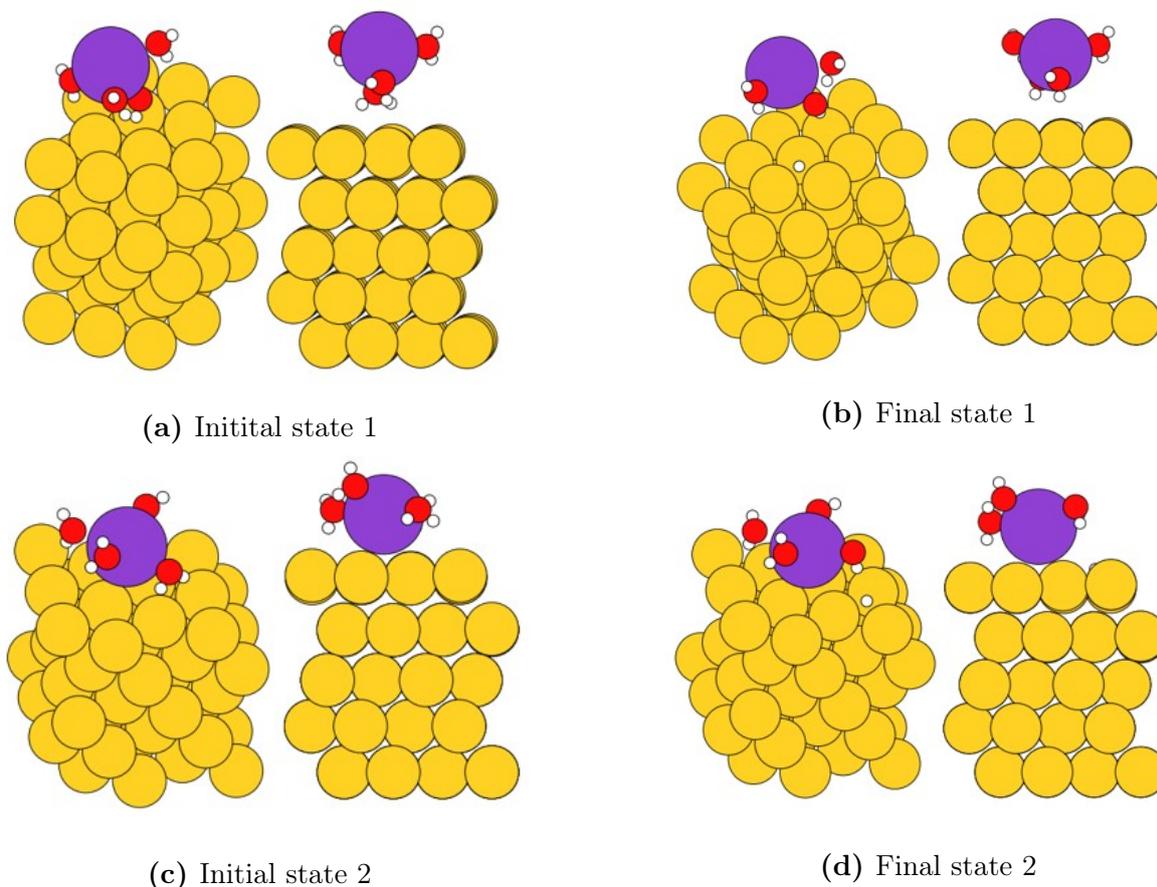


Figure 29: Optimized structures with potassium. Potential is 0 V versus reference hydrogen electrode. Essentially two different structures were obtained. One with the potassium floating on the surface (structure 1) one with potassium sticking on the surface (structure 2).

7.4.2 Structures and NEB and in -0.5 V

The potassium structures were also optimized at a potential of -0.5 V. These structures are in Figure 30. In the Table 3 are again the reaction energies and the number of excess electrons. Energies are lower by 0.43 eV and 0.41 eV, so the reaction becomes thermodynamically more favorable, which is again expected due to the more reductive potential.

NEB calculations were also performed to find the activation energy of the reaction in the potential -0.5 V. A The energy and the number of excess electrons are plotted like previously in the figure 31 using now the second structure as representative. The activation energies are shown in Table 3. We can also see that the activation energy has decreased. It could be noted that the proton seems to move over another smaller barrier when moving

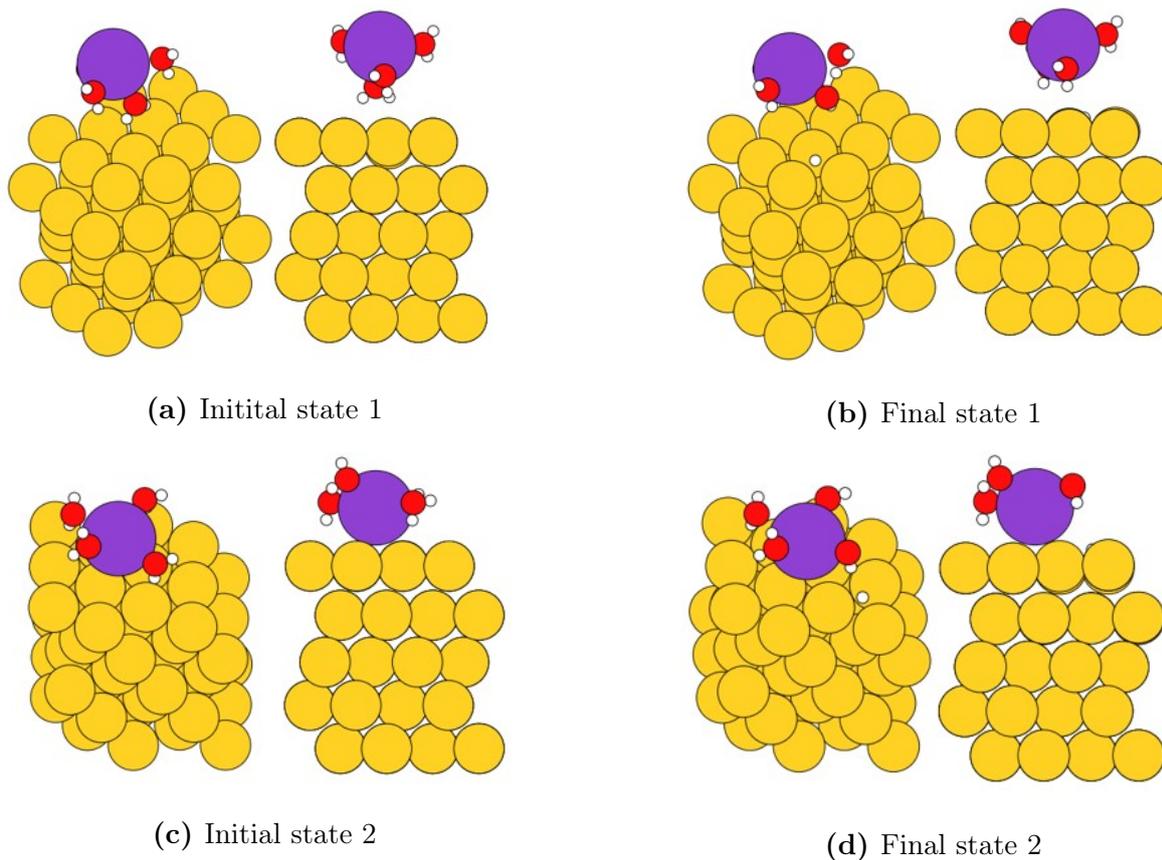


Figure 30: Optimized structures with potassium. Potential is -0.5 V versus reference hydrogen electrode. Same structures as previous were considered.

in the hollow site of the gold. Again, the decrease in activation energy and reaction energy is in agreement with the literature^{11,45} due to the more reductive potentials.

Table 3: The computed reaction energy, change in the number of electrons, and activation energies as a function of the electrode potential for the Volmer step on Au(111) in the presence of K^+ .

	Reaction energy (eV)	Change in the number of excess electrons	Activation energy (eV)
potassium 1 at 0 V	0.77	1.48	1.12
potassium 2 at 0 V	1.12	1.77	1.42
potassium 1 at -0.5 V	0.34	1.40	0.88
potassium 2 at -0.5 V	0.71	1.65	1.04

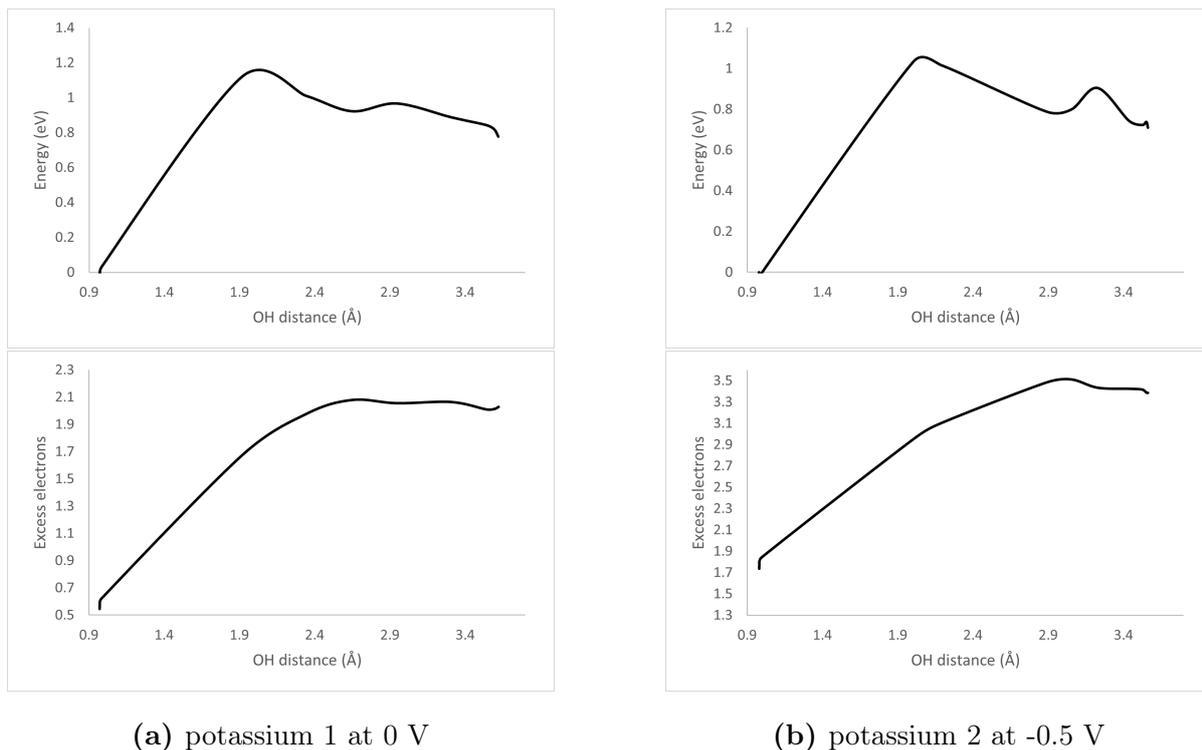


Figure 31: Representative energy diagrams and evolutions of excess electron for potassium. Activation energies was obtained from these as a difference of energies of initial and transition state. Change in the number of excess electrons were monitored to see it increases smoothly to from value of initial state to value of final state.

7.5 Summary of the results

Table 4 now summarizes all previous results. Here, we can again conclude the main details. The dissociation of water without the cations is not thermodynamically favorable compared to the presence of a cation. Cesium could have been interesting to investigate further, but a suitable computational model could not be identified to find optimal initial and final states for the purposes of this thesis. The results show that that all considered cations have have a significant effect on the reaction energy possibility of lowering it by more than 1 eV. Making the potential more reductive could decrease the reaction energy by around 0.40 eV and the activation energy by around 0.30 eV making the reaction more favorable at more reducing potentials. Now we can also compare lithium and potassium. From the reaction energies, it is not clearly seen which cation would be more active for the alkaline hydrogen evolution reaction, but the activation energies seem to be lower for lithium. Since the reaction energies could not tell the difference, we can deduce that the bond energy theory, considered in Section 4.1, could not explain the effects of the ions,

but we recall from Figure 13 that potassium was found experimentally to be more active towards hydrogen evolution. On the other hand the kinetic theory, considered in Section 4.3, seems to even give the opposite result since the activation energy is generally lower for lithium. These are considered more in the conclusions.

Table 4: Summary of the calculated results

	Reaction energy (eV)	Change in the number of excess electrons	Activation energy (eV)
water	2.17	1.83	-
cesium 1	0.18	1.41	-
cesium 2	0.90	0.26	-
lithium 1 at 0 V	0.83	1.41	1.11
lithium 2 at 0 V	0.77	1.39	1.08
lithium 1 at -0.5 V	0.27	1.44	0.79
lithium 2 at -0.5 V	0.83	1.28	0.79
lithium 1 at -0.5 V with adsorbed hydrogen	0.37	1.46	0.74
potassium 1 at 0 V	0.77	1.48	1.12
potassium 2 at 0 V	1.12	1.77	1.42
potassium 1 at -0.5 V	0.34	1.40	0.88
potassium 2 at -0.5 V	0.71	1.65	1.04

7.6 Towards the more general kinetic theory of the hydrogen evolution on gold: Potential energy surface for adiabatic OH dissociation

All results in the previous sections were for a fully classical and adiabatic hydrogen evolution. To move towards treating the adiabatic tunneling mechanism within the general kinetic theory, we next study the generation of adiabatic protonic states depicted in Figure 10a for hydrogen evolution. In practice, the energy of transferring the proton from water to the surface was computed in a geometry where the solvent has reorganized to its transition state geometry. This theory was also considered in my Bachelor's thesis.³³ Here the transition state of the second lithium structure was chosen to compute the energy

plot when the proton moves to the surface. Basically, all the other atoms were kept in place, and the proton was moved up and down perpendicular to the surface, and energy was plotted as a function of the distance to the oxygen in which it deprotonates. The script is in the Appendix. Plotting gives similar type of plot as in the Section 3.2 and with the more detailed kinetic theory tunneling probabilities could be calculated from the plot. It gives the plot shown in Figure 32. The fourth-degree polynomial was also fitted and used as in the Bachelor's Thesis³³ In the future, these adiabatic proton curves will serve as a starting point for studying nuclear tunneling and also vibronic nonadiabaticity.¹⁶

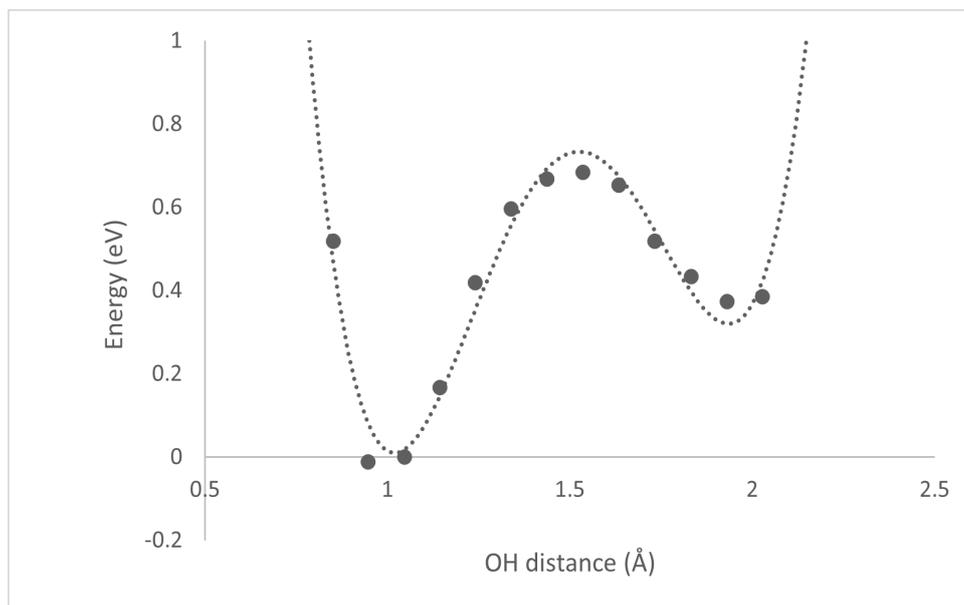


Figure 32: Energy of the proton plotted against its distance to oxygen in the transition state of lithium 1 structure by keeping other atoms fixed. Plot is similar as in the Section 3.2 and with the kinetic theory tunneling probabilities could be calculated from the plot to understand kinetics more deeply.

8 Conclusions

The hydrogen evolution is an important reaction in electrocatalysis as shown in Figure 2 and it is experimentally known that different alkali metals have different effects in the reaction, but it is not yet understood why this is the case. The hydrogen evolution is also an example of the proton-coupled electron transfer reaction and also understanding of these processes is far from clear, although research has advanced quite rapidly. The proton-coupled electron transfer in general is challenging because of possible nuclear quantum effects and nonadiabaticity of the reaction, and hydrogen evolution is not an exception.

When considering the hydrogen evolution, it is also unclear how different electrochemical properties such as the role of the electrolyte, electrode, pH, and electrical double layer affect the progression of the reaction. This also makes accurate modeling of the reaction particularly difficult. Electrode potential, electrolyte, pH, electrostatic interactions, etc. all are important to consider. The main interest of this thesis was to investigate the effects of alkali metal cations on the hydrogen evolution in water splitting on the metal surface.

In the computational work the thesis used the grand canonical density functional theory and solvent jellium model to model the hydrogen evolution on the gold electrode without ions and in the presence of a lithium, potassium or cesium ion. The situation without the ion and in the presence of the cesium ion was investigated briefly since without ion reaction was not thermodynamically favourable and finding optimal initial and final state for the cesium proved to be difficult for the purposes of this thesis. Structure optimization of the initial and final states showed that the reaction was endothermic for all the cases and, in particular, that the ion makes the reaction thermodynamically more favorable. Also, the change in potential to more reductive made the reaction more thermodynamically favorable. The reaction energies did not give clear differences between the ions. Then the NEB calculations for lithium and potassium generally gave lower activation energies for lithium.

Since the reaction energies could not tell the difference between the lithium and potassium ions and with the activation energies could even give the opposite result in contrast to Figure 13. By these it seems that at least the bond energy theory from Section 4.1 and the kinetic theory from Section 4.3 could not explain the difference, since the bond

energy theory considers only the thermodynamics, that comes from the reaction energy, and kinetic theory kinetic that comes from the activation energy. The kinetic theory could, though, still have its defense since with the methods of the thesis the mechanism is adiabatic, so a nonadiabatic mechanism could still explain the results. In some sense it could though be expected that the single number could not describe such a complicated system like an electrochemical system.

There are also other possibilities to consider. It is, of course, possible that the model or the mechanism is incomplete, meaning that the structures for initial and final states are too simple. This is especially possible for potassium and cesium since the ions are large, so they can fit a lot of water around them. However, lithium, as a small ion, does seem to have the right description. Also the double layer theory of Section 4.2 was taken in account by implicit-explicit solvent, ions, pH and electrode, but with the compromises since the dynamics and reorganisation is missing. It is possible that the role of the electrolyte is dynamic, and modeling the reaction would require molecular dynamics. This is also a possibility for why potassium and cesium could be too simple, since there is a lot of room to move around them.

The thesis still manages to show that ions indeed effect the thermodynamics and kinetics of hydrogen evolution, and without ions description is not correct. Also, it is important to note that this model is already quite complicated and takes into account the bond energy theory, the double layer theory and the kinetic theory with compromises. It could still not explain the experiments, so this indeed shows that the model needs to be further improved. Considering dynamics, reorganization or nonadiabatic mechanism could be ways to make the model better. With them it could be possible to explain the effects of the alkali metal ions to hydrogen evolution.

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Appendix

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```

from ase import *
from ase.io import read, PickleTrajectory
from ase.optimize import FIRE, BFGS
from gpaw.utilities import h2gpts
from ase.units import mol, kJ, kcal, Pascal, m
from ase.data.vdw import vdw_radii
from ase.parallel import parprint, rank, size
from gpaw.utilities import h2gpts
from gpaw import *
from gpaw.analyse.hirshfeld import HirshfeldPartitioning
from gpaw.analyse.vdwradii import vdWradii
from ase.calculators.vdwcorrection import vdWtkatchenko09pr1
from gpaw.utilities.timing import ParallelTimer
from gpaw.poisson import PoissonSolver
from ase.neb import *
# Import solvation modules
import sys, os
from ase.units import mol, kJ, kcal, Pascal, m

from gpaw.solvation import (
    SolvationGPAW,           # the solvation calculator
    EffectivePotentialCavity, # cavity using an effective potential
    Powerl2Potential,       # a specific effective potential
    LinearDielectric,       # rule to construct permittivity function from the cavity
    GradientSurface,        # rule to calculate the surface area from the cavity
    SurfaceInteraction       # rule to calculate non-electrostatic interactions
)

from gpaw.solvation.sjm import SJM, SJMPowerl2Potential

atoms = read('Li_initial_-0.5_opt.traj')

tag = 'Li_initial_-0.5_opt2'

#####
# set the potential
#####
E_target_RHE = - 0.5
pH = 13
E_target_SHE = E_target_RHE - 0.059*pH
E_pzc_comp = 5.02 # absolute wrt continuum, computed
E_pzc_exp = 0.559 # vs SHE, Experimental
E_ref_comp_SHE = E_pzc_comp - E_pzc_exp # computational reference potential wrt RHE

E_target = E_ref_comp_SHE + E_target_SHE

# Solvent parameters

u0 = 0.180 # eV
epsinf = 78.36 # Dielectric constant of water at 298 K
gamma = 18.4 * 1e-3 * Pascal * m
T = 298.15 # K
vdw_radii = vdw_radii.copy()
vdw_radii[79] = 2 #Au
atomic_radii = lambda atoms: [vdw_radii[n] for n in atoms.numbers]

# define the neb and specify charges
calc = SJM(h=0.18,
            spinpol = False,
            basis = 'dzp',
            #mode='lcao',
            xc = 'BEEF-vdW',
            maxiter=500,
            nbands = -40,
            symmetry = 'off',
            eigensolver = Davidson(3),
            kpts = (4,4,1),
            poissonsolver={'dipolelayer': 'xy'},
            occupations = FermiDirac(width = 0.05),
            mixer = Mixer(beta = 0.05, nmaxold = 5, weight=90.0),
            convergence = {'eigenstates': 1.0e-4, # eV^2 / electron
                           'energy': 1.0e-5, # eV / electron
                           'density': 1.0e-4},
            txt = '%s.txt'%tag, #verbose=True,
            potential=E_target,

```

```
dspot=0.025,
doublelayer={'upper_limit':atoms.get_cell()[2][2]-1,
             'start':'cavity_like'},
cavity=EffectivePotentialCavity(
    effective_potential=SJMPower12Potential(atomic_radii, u0,
    unsolv_backside=False, H2O_layer=False),
    temperature=T,
    surface_calculator=GradientSurface()),
dielectric=LinearDielectric(epsinf=epsinf),
interactions=[SurfaceInteraction(surface_tension=gamma)])

atoms.set_calculator(calc)
atoms.get_potential_energy()
relax = BFGS(atoms, logfile='%s.log'%tag, trajectory='%s.traj'%tag)
relax.run(fmax=0.05)
```

```

from ase import *
from ase.io import read, PickleTrajectory
from ase.optimize import FIRE, BFGS
from gpaw.utilities import h2gpts
from ase.units import mol, kJ, kcal, Pascal, m
from ase.data.vdw import vdw_radii
from ase.parallel import parprint, rank, size
from gpaw.utilities import h2gpts
from gpaw import *
from gpaw.analyse.hirshfeld import HirshfeldPartitioning
from gpaw.analyse.vdwradii import vdWradii
from ase.calculators.vdwcorrection import vdWtkatchenko09pr1
from gpaw.utilities.timing import ParallelTimer
from gpaw.poisson import PoissonSolver
from ase.neb import *
# Import solvation modules
import sys, os
from ase.units import mol, kJ, kcal, Pascal, m

from gpaw.solvation import (
    SolvationGPAW,           # the solvation calculator
    EffectivePotentialCavity, # cavity using an effective potential
    Powerl2Potential,       # a specific effective potential
    LinearDielectric,       # rule to construct permittivity function from the cavity
    GradientSurface,        # rule to calculate the surface area from the cavity
    SurfaceInteraction       # rule to calculate non-electrostatic interactions
)

from gpaw.solvation.sjm import SJM, SJMPowerl2Potential

# define the neb and specify charges
tag = 'Li_i10_-0.5_2' #name for your neb trajectory
nimages = 10 #number of images

'''
images = []
initial = read('Li_initial_-0.5_opt2.traj') #reads the geometry of the initial state (reactants)
final = read('Li_final_-0.5_opt.traj') #reads the geometry of the final state (products)
'''

images = read('CINEB_Li_i10_-0.5.traj@-12:')

'''
images.append(initial)

for i in range(nimages):
    images.append(initial.copy())
images.append(final)

neb = NEB(images, parallel=False)
neb.interpolate('idpp') #method to create geometries in between
images = neb.images.copy()
'''

#####
# set the potential
#####
E_target_RHE = - 0.5
pH = 13
E_target_SHE = E_target_RHE - 0.059*pH
E_pzc_comp = 5.02 # absolute wrt continuum, computed
E_pzc_exp = 0.559 # vs SHE, Experimental
E_ref_comp_SHE = E_pzc_comp - E_pzc_exp # computational reference potential wrt RHE

E_target = E_ref_comp_SHE + E_target_SHE

# Solvent parameters

u0 = 0.180 # eV
epsinf = 78.36 # Dielectric constant of water at 298 K
gamma = 18.4 * 1e-3 * Pascal * m
T = 298.15 # K
vdw_radii = vdw_radii.copy()
vdw_radii[79] = 2 #Au

```

```

atomic_radii = lambda atoms: [vdw_radii[n] for n in atoms.numbers]

n = size//nimages
j = 1 + rank//n
assert nimages*n==size

# define the neb and specify charges
def set_calc(atoms, txt, communicator):
    calc = SJM(h=0.18,
              spinpol = False,
              basis = 'dzp',
              #mode='lcao',
              xc = 'BEEF-vdW',
              maxiter=1000,
              nbands = -40,
              symmetry = 'off',
              txt=txt,
              communicator=communicator,
              eigensolver = Davidson(3),
              kpts = (4,4,1),
              poissonsolver={'dipolelayer': 'xy'},
              occupations = FermiDirac(width = 0.05),
              mixer = Mixer(beta = 0.05, nmaxold = 5, weight=90.0),
              convergence = {'eigenstates': 1.0e-4, # eV^2 / electron
                             'energy': 1.0e-5, # eV / electron
                             'density': 1.0e-4},
              #verbose=True,
              potential=E_target,
              dpot=0.025,
              doublelayer={'upper_limit':atoms.get_cell()[2][2]-1,
                           'start':'cavity_like'},
              cavity=EffectivePotentialCavity(
                  effective_potential=SJMpower12Potential(atomic_radii, u0,
                  unsolv_backside=False, H2O_layer=False),
                  temperature=T,
                  surface_calculator=GradientSurface()),
              dielectric=LinearDielectric(epsinf=epsinf),
              interactions=[SurfaceInteraction(surface_tension=gamma)])

    atoms.set_calculator(calc)
    atoms.get_potential_energy()

for i in range(nimages):
    ranks = np.arange(i*n, (i+1)*n)
    if rank in ranks:
        set_calc(images[i+1], txt='%d_new.txt'%i, communicator=ranks)

# NEB calculations
'''
neb = NEB(images, parallel=True, method='eb')
relax = BFGS(neb, logfile='NEB_%s.log'%tag, trajectory='NEB_%s.traj'%tag)
relax.run(fmax=0.5, steps=20)
'''

#Climbing image neb calculations to find transition stateci
cineb = NEB(images, parallel=True, method='eb', climb=True)
relax = FIRE(cineb, logfile='CINEB_%s.log'%tag, trajectory='CINEB_%s.traj'%tag)
relax.run(fmax=0.10)

```



```
        'density': 1.0e-4},
txt = '%s.txt'%tag, #verbose=True,
potential=E_target,
dpot=0.025,
doublelayer={'upper_limit':atoms.get_cell()[2][2]-1,
             'start':'cavity_like'},
cavity=EffectivePotentialCavity(
    effective_potential=SJMpower12Potential(atomic_radii, u0,
    unsolv_backside=False, H2O_layer=False),
    temperature=T,
    surface_calculator=GradientSurface()),
dielectric=LinearDielectric(epsinf=epsinf),
interactions=[SurfaceInteraction(surface_tension=gamma)])

atoms.calc = calc
traj = Trajectory('binding_curve.traj3', 'w')

step = 0.1
nsteps = 3

for i in range(nsteps):
    d = 2.564 + i*step
    atoms.positions[66, 2] = atoms.positions[52, 2] + d
    e = atoms.get_potential_energy()
    print('distance, energy', d, e)
    traj.write(atoms)

energies = []
distances = []

for atoms in iread('binding_curve.traj'):
    energies.append(atoms.get_potential_energy())
    distances.append(atoms.positions[66, 2] - atoms.positions[52, 2])

print(distances, energies)
```