Hydrogen Evolution Reaction on Carbon Nanotubes: Insights from Electronic Structure Theory

Nico Holmberg
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Nico Holmberg

A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Chemical Engineering, at a public examination held at the lecture hall KE1 of the school on 23 November 2018 at 12.

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Abstract

Simulations based on density functional theory (DFT) are a valuable complementary tool to experiments because they can provide atomistic level insight into the origins of electrocatalytic activity, a domain largely inaccessible by experiments. In practice, the accuracy of such simulations is, however, hindered by both fundamental theoretical issues and the limitations of computational resources. These challenges were critically investigated in this thesis in order to create a transferable and sufficiently comprehensive kinetic model for carbon nanotube (CNT) catalyzed hydrogen evolution (HER), which can quantify the effects of nanotube doping without resorting to direct experimental input. Hydrogen coverage, electrode potential, and solvation were deemed the most crucial variables to include in kinetic HER models.

A baseline for the HER reactivity of pristine CNTs was established using the developed model. The Volmer-Heyrovsky mechanism was determined to be the predominant reaction mechanism on CNTs with the latter step being rate limiting. The inability of pristine CNT to efficiently catalyze HER was demonstrated by comparison to theoretical work on platinum. Introducing a substitutional nitrogen dopant did not result in the activation of the nearest carbon site, although a descriptor model based on adsorption energies would have suggested otherwise. By contrast, the formation of carbon 5-ring structures led to a notable activity enhancement on open-ended CNTs. The improvement was attributed to ring strain which could indicate that 5-rings found also in, e.g., fullerenes are inherently more active than regular 6-rings.

The accuracy of DFT-computed activation and reaction energies were assessed by switching to an alternative theoretical framework where the reaction is described in terms of diabatic electronic states, in analogy to Marcus theory of electron transfer. This approach should mitigate spurious electron delocalization effects often plaguing DFT. Constrained DFT (CDFT) methods were implemented in this thesis to perform such simulations. The results indicated that conventional DFT not only underestimated barriers but also overestimated reaction energies. Adapting this framework more extensively was identified as an appealing future research direction.

Prior to this study, the CDFT implementation was validated by reproducing reference results for gas phase charge transfer reactions. In a stringent test of the implementation’s efficiency, the Marcus electron transfer parameters of a mixed-valence compound were then evaluated. To that end, a condensed phase CDFT molecular dynamics simulation was performed where the charge-localized reactant and product states were continuously monitored, which had not been attempted previously at the full electronic structure level. Marcus parameters were obtained as trajectory averages of the vertical energy gap and the electronic coupling, yielding values in satisfactory agreement with experiments and underlining the importance of accounting for explicit solvation.

Keywords  Density Functional Theory, Electrocatalysis, Hydrogen Evolution Reaction, Diabetic Electronic State, Carbon Nanotube

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Preface

This thesis is the culmination of my four years of research at the Department of Chemistry and Materials Science at Aalto University School of Chemical Engineering. The work has been funded by Aalto University School of Chemical Engineering through a Ph.D. scholarship and the Academy of Finland through its Centres of Excellence program, project no. 251748. I am grateful to CSC–IT Center for Science, Finland, and the Swiss National Supercomputing Centre (CSCS) for their generous allocations of computing resources and for their technical expertise, which both were instrumental for the completion of this thesis.

First and foremost, I wish to thank Professor Kari Laasonen for giving me the opportunity to pursue a doctoral degree in computational electrochemistry—an interesting and versatile topic that I found very motivating to work on due to the challenges it offered. I thoroughly enjoyed the freedom he gave me to define my own research, while at the same being there ready to offer guidance and ideas whenever I felt I was at an impasse. I also wish to thank Professor Tanja Kallio for a fruitful collaboration on a joint experimental-computational project, which gave me a fresh perspective on electrocatalyst design.

I am grateful to the CP2K developer community for their assistance in the development of constrained DFT methods in CP2K. In particular, I wish to acknowledge the contribution of Iain Bethune at the STFC Hartree Centre (formerly at the University of Edinburgh) in tracking down some bugs and helping me get started with regular contributions to CP2K development. I also want to thank him for inviting me to the CP2K-UK 2018 workshop to give a tutorial lecture on our work on CDFT and for arranging travel funding through EPCC.

I wish to thank my fellow doctoral candidates, past and present, for creating a relaxed atmosphere in- and outside the workplace. My special thanks go to Sampsa for his help with the classical simulations performed in this thesis and for all the discussions we’ve had over the years in our shared office. I also want to thank Miikka and Sami for motivating me to take up triathlon which became my go-to method for unwinding.
Last, but certainly not the least, I want to express my gratitude to my family for their love and support during this thesis. Mari, our adventures together have been the highlight of my life so far.

Espoo, October 23, 2018,

Nico Holmberg
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This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


Author’s Contribution

Publication I: “Ab Initio Electrochemistry: Exploring the Hydrogen Evolution Reaction on Carbon Nanotubes”

NH planned the simulations together with KL. NH surveyed the literature, performed all simulations, and analyzed the results. KL supervised the research and critically reviewed the results and conclusions. NH wrote the manuscript in collaboration with KL.

Publication II: “Theoretical Insight into the Hydrogen Evolution Activity of Open-Ended Carbon Nanotubes”

NH planned the simulations together with KL. NH surveyed the literature, performed all simulations, and analyzed the results. KL supervised the research and critically reviewed the results and conclusions. NH wrote the manuscript in collaboration with KL.

Publication III: “Efficient Constrained Density Functional Theory Implementation for Simulation of Condensed Phase Electron Transfer Reactions”

NH implemented the simulation methods, surveyed the literature, planned and performed all simulations, and analyzed the results. KL supervised the research and critically reviewed the results and conclusions. NH wrote the manuscript in collaboration with KL.
Author’s Contribution

Publication IV: “Diabatic model for electrochemical hydrogen evolution based on constrained DFT configuration interaction”

NH implemented* the simulation methods, surveyed the literature, planned and performed all simulations, and analyzed the results. KL supervised the research and critically reviewed the results and conclusions. NH wrote the manuscript in collaboration with KL.

* Simulation software

The simulation methods described in Publications III-IV were implemented in the open-source quantum chemistry software CP2K, which is freely available for download online at https://www.cp2k.org.
## Abbreviations

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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>AO / MO / HOMO</td>
<td>Atomic / Molecular Orbital / Highest Occupied MO</td>
</tr>
<tr>
<td>CHE / SHE</td>
<td>Computational / Standard Hydrogen Electrode</td>
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<td>CI</td>
<td>Configuration Interaction</td>
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<tr>
<td>CNT / NCNT</td>
<td>Carbon Nanotube / Nitrogen-Doped CNT</td>
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<tr>
<td>DFT / CDFT</td>
<td>Density Functional Theory / Constrained DFT</td>
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<tr>
<td>DIIS</td>
<td>Direct Inversion in the Iterative Subspace</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of (Electronic) States</td>
</tr>
<tr>
<td>ET / HT / PT</td>
<td>Electron / Hydrogen Atom / Proton Transfer</td>
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<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
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<td>GPW</td>
<td>Gaussian and Planewaves</td>
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<tr>
<td>GTO</td>
<td>Gaussian-Type Orbital</td>
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<td>HER</td>
<td>Hydrogen Evolution Reaction</td>
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<tr>
<td>IS / FS</td>
<td>Initial (Reactant) / Final (Product) State</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham</td>
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<tr>
<td>MEP</td>
<td>Minimum Energy Path</td>
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<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
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<tr>
<td>NEB</td>
<td>Nudged Elastic Band</td>
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<tr>
<td>OT</td>
<td>Orbital Transformation</td>
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<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
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<td>PCET</td>
<td>Proton-Coupled Electron Transfer</td>
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<tr>
<td>SIE</td>
<td>Self-Interaction Error</td>
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<tr>
<td>SHS</td>
<td>Soudackov–Hammes-Schiffer</td>
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<td>SCF</td>
<td>Self-Consistent Field</td>
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Symbols

\textbf{C} \quad \text{Coefficient Matrix}

\textit{e} \quad \text{Elementary Charge}

\textit{E} \quad \text{Energy}

\textbf{F} \quad \text{Force}

\textit{G} / \Omega \quad \text{Gibbs / Landau Free Energy}

\textit{G} \quad \text{Reciprocal Space Lattice Vectors}

\textbf{H} \quad \text{Hamiltonian Matrix}

\hat{\mathbf{H}} \quad \text{Hamiltonian Operator}

|H_{ab}| \quad \text{Electronic Coupling}

\textit{j} \quad \text{Current Density}

\textbf{J} \quad \text{Jacobian Matrix}

\textit{k} \quad \text{Reaction Rate Constant}

\textit{k}_B \quad \text{Boltzmann Constant}

\textbf{K} \quad \text{Kohn-Sham Matrix}

\textit{r} \quad \text{Electron Coordinate}

\textbf{R} \quad \text{Nuclear Coordinate}

\textit{S} \quad \text{Entropy}

\textbf{S} \quad \text{Overlap Matrix}

\textit{T} \quad \text{Temperature}

\textit{U} \quad \text{Electrode Potential}

\textit{v} \quad \text{Potential}

\textit{w} \quad \text{Weight Function}

\epsilon / \varepsilon \quad \text{Orbital Energy / Convergence Threshold}

\eta \quad \text{Overpotential}

\theta \quad \text{Coverage}

\lambda \quad \text{Solvent Reorganization Energy}

\mu \quad \text{Fermi level}

\xi \quad \text{Lagrange Multiplier}

\rho \quad \text{Electron Density}

\sigma \quad \text{Spin Variable}

\Phi / \phi \quad \text{Workfunction / Volta (Outer) Potential}

\Psi / \psi \quad \text{Many- / One-Electron Wavefunction}
1. Introduction

Electronic structure simulations, in particular, approaches based on density functional theory (DFT) have emerged as a valuable complementary tool to experimental techniques in electrocatalysis research within the past few decades, spurred by rapid advances in computing power and numerical algorithms. Although computational methods are unlikely to supersede experiments in the foreseeable future, numerical simulations can, and will in growing capacity continue to, provide valuable insight into the atomic-scale origins of electrochemical reactivity, a domain that is largely inaccessible by experimental methods. Ultimately, a better understanding of the electronic phenomena involved in catalytic processes will aid in tailoring better performing catalyst materials.

Within the field of electrocatalysis, computational efforts have primarily concentrated on two topical and technologically relevant reactions, namely, the hydrogen evolution (HER), \(2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})\), and water oxidation reactions. These reactions form the half-reactions of the electrochemical water splitting reaction, which is an environmentally friendly process to produce hydrogen from excess electricity when sourced from renewable sources. Using hydrogen as an alternative zero emission fuel in the transportation of goods and people is a prospective step toward transitioning into a more sustainable society, as transportation accounts for a sizable fraction of total greenhouse gas emissions.

Scarcе noble metals, such as Pt, are commonly used as HER catalysts due to their superior activity properties. Replacing them with more abundant and sufficiently active alternative materials remains one of the major obstacles preventing the widespread adoption of water electrolyzers. A class of materials that have received substantial attention in this regard are carbon nanotubes (CNTs) and other carbon-based nanomaterials. Pristine CNTs are known to be poor HER catalysts, but modifying them through heteroatom doping or other modification techniques can vastly improve their inherent activity. Other approaches to higher activity include using CNTs as high surface area nanoparticle supports to reduce catalyst loading, or using them as protective shells around nanoparticles that would otherwise oxidize at electrochemical conditions.

The theoretical modeling of HER and other electrocatalytic reactions is challenging due to the unique complexity of the catalytic environment, where re-
actions occur at the solid-liquid interface between the catalyst and the electrochemical double layer. Additional complicating factors include the need to account for electrode potential and other external variables. Capturing all of these phenomena at a consistent level of theory is impossible, at least at present, suggesting that actual simulations must resort to numerous simplifications to make the system computationally tractable. Comprehensive kinetic studies of HER are, therefore, understandably quite scarce, with main efforts focused on characterizing Pt and other well-defined metal surfaces. The approaches proposed to model metals do not readily generalize to carbon nanotube catalysts because CNTs are highly heterogeneous, hindering direct comparisons between simulations and experiments. This fundamental issue has received very little attention in prior theoretical studies of HER on CNTs and certainly has not been addressed adequately enough to allow justifying why some functionalizations lead to enhanced experimental activity, while others do not.

The accuracy of DFT models is not only impaired by the necessity to simplify the system but also by inherent theoretical limitations. Creating more accurate models of electrocatalysis, which might eventually lead to the discovery of better catalysts, is impossible without addressing these issues. Combining other theoretical frameworks with DFT is one potential remedy for improving accuracy. A particularly appealing class of methods are charge transfer theories based on localized (diabatic) electronic states, such as the renowned Marcus theory of electron transfer, since they provide a natural means to eliminate spurious electron delocalization effects, often plaguing DFT simulations. They are also suitable for investigating phenomena that are not directly accessible by conventional DFT methods, providing a fresh perspective on electrocatalysis.

The issues highlighted above served as guidelines during the completion of this thesis project, whose main research objectives can thus be stated as follows

**Q1.** Identify theoretical challenges in modeling electrocatalytic reactions from the perspective of HER. Review approaches proposed to tackle these issues.

**Q2.** Develop transferable and sufficiently comprehensive scheme to model the HER reactivity of carbon nanotubes. Using a pristine CNT as the baseline, consider the impact of simple functionalizations on reactivity.

**Q3.** Explore applicability of diabatic charge transfer theories to electrocatalysis. Implement a method to utilize them within the same computational framework used in the simulations of HER on carbon nanotubes (Q2).

This thesis is structured into a summary part, Chapters 2-5, and an appendix which consists of four peer-reviewed articles. Computational approaches to modeling HER and associated challenges are outlined in Chap. 2. Density functional theory, its limitations, and a method to mitigate some of these errors are introduced in Chap. 3. The main results of this thesis are presented in Chap. 4. A brief summary is given in Chap. 5 including suggestions for future work.
2. Computational Models of Hydrogen Evolution

Two prevalent research paradigms have been adopted in the field of computational electrochemistry to tackle the challenge of discovering new catalysts.\textsuperscript{1,11,17} These paradigms, namely, the descriptor-\textsuperscript{18–21} and kinetics-based\textsuperscript{8,22–24} methods are ultimately complementary to each other;\textsuperscript{25} however, their vastly different practical approach to catalysis modeling makes them better suited to different specific tasks. To elucidate these differences, the main aspects of these methods will be discussed and contrasted in Sec. 2.1, motivating the need to adopt the kinetic modeling paradigm to investigate the effects of functionalization on the HER activity of carbon nanotubes. Other methods will also be highlighted briefly, but an in-depth discussion about the specifics is beyond the scope of this thesis. Subsequently, a more thorough description of kinetic simulations will be presented in Sec. 2.2, where an emphasis will be placed on the unique issues associated with describing electrochemical reactions.

2.1 The Descriptor and Kinetic Models to Catalyst Design

The descriptor model is based on the simple premise that the electrocatalytic activity of any material should be characterizable by a reduced set of easily calculable variables.\textsuperscript{1,18,19} These variables should be universal and transferable, i.e., they should be able to ascertain differences in catalytic performance in a range of different types of materials. Deriving such variables for HER is complicated by the fact that the reaction may proceed through two competing mechanisms, the Volmer-Heyrovsky and Volmer-Tafel mechanisms. The predominant mechanism and the rate-limiting step are material-dependent, which can also vary as a function of the reaction conditions. Focusing on HER in acidic media and denoting a vacant surface site as $\ast$, the mechanisms are comprised of the elementary steps

\begin{align*}
H^+(aq) + \ast + e^- &\rightarrow H^* \quad \text{(Volmer)} \\
H^+(aq) + H^* + e^- &\rightarrow H_2(g) + \ast \quad \text{(Heyrovsky)} \\
2 H^* &\rightarrow H_2(g) + 2 \ast \quad \text{(Tafel)}
\end{align*}
Both experimental and computational estimates of catalytic activity can be employed to construct a descriptor model. The use of experimental quantities is, however, more frequent than computational ones, at least in regards to HER. Experiment-based models will, therefore, be the main focus of this thesis. The most commonly used figure of merit for HER catalysis is the so-called standard exchange current density, $j_0$, defined as the measured current density, $j$, for unit concentrations of reactants when the hydrogen evolution and oxidation reactions (the reverse reaction of HER) are in equilibrium, that is, their rates are equal but nonzero.\footnote{This metric is not the only measure of catalytic performance and, in fact, it can be argued that $j_0$ is perhaps not even the best metric for an actual electrochemical device operating at an electrode potential, $U$, different from the equilibrium potential, $U^\circ$.}\footnote{27–29} Other factors that should be taken into account in the design of electrocatalysts include:\footnote{27–29}

- the onset potential, which is defined as the minimum overpotential $U - U^\circ$ needed to obtain a measurable current due to HER
- the overpotential needed to achieve a fixed current density, usually $j = 10$ mA cm$^{-2}$ normalized by the geometric area of the electrode
- the Tafel slope, which describes how the reaction rate changes with potential and provides insight into the reaction mechanism
- the Faradaic efficiency indicating how selective the catalyst is toward HER, measured as the fraction of current that went into producing H$_2$(g)
- long-term stability, i.e., the drift of current density at fixed potential

Although maximizing activity has been the main objective of descriptor models thus far,\footnote{1} the inclusion of multiple experimental measures of what constitutes a “good” catalyst could benefit endeavors to construct more comprehensive models, which ultimately will necessitate the introduction of new descriptors in addition to the traditional ones utilized in conjunction with HER (see below).\footnote{20,30,31}

In practice, the descriptor-based model for catalysis design first involves computing the values of the selected descriptor quantities for a group of structurally well-defined materials. Volcano-shaped curves are often acquired once the experimental activity of these materials is plotted against the descriptors. These aptly named volcano plots indicate the range of values for the descriptors where catalytic performance is maximized, thus providing a clear target for computational studies to pursue. New catalyst candidates can subsequently be screened from a larger set of materials by evaluating the values of the descriptors.\footnote{1,18,19}

If the screening procedure unveils a potentially active catalyst, the final stage of the procedure involves synthesizing and characterizing the material, followed by rigorous validation of activity, stability and other properties. One remarkable success story of this method was the discovery of HER active edge sites in MoS$_2$ nanoparticles and the activation of MoS$_2$ basal planes through the introduction of strain and vacancies, despite the poor catalytic properties of bulk MoS$_2$.\footnote{32–36}

By far the most widely employed descriptor is the adsorption free energy of hydrogen, defined as the free energy change $\Delta G_{ads}^H$ related to the reaction $\frac{1}{2}$ H$_2$(g) + * → H$^*$, where H$_2$ is at standard conditions and it is assumed to be in
Computational Models of Hydrogen Evolution

equilibrium with a pH = 0 solution.\textsuperscript{18,37} This expression can be evaluated as

$$
\Delta G^H_{\text{ads}} = \Delta E^H_{\text{ads}} + \Delta ZPE^H_{\text{ads}} - T \Delta S^H_{\text{ads}}
$$

(2.4)

where the first term is the adsorption energy of hydrogen, the second term is a zero-point vibrational energy correction, and the final term is an entropic correction. The hydrogen adsorption energy is defined as $\Delta E^H_{\text{ads}} = E_{H^*} - E_* - \frac{1}{2} E_{H_2(g)}$, where $E_{H^*}$ is the energy of the surface with 1 adsorbed hydrogen, $E_*$ the energy of the bare surface and $E_{H_2(g)}$ the energy of gas phase hydrogen. The correction terms can be evaluated from a vibrational normal mode analysis combined with statistical mechanics and tabulated reference data, amounting to roughly constant shift $+0.24$ eV of the electronic energies irrespective of the actual surface that binds hydrogen.\textsuperscript{37} The adsorption of multiple hydrogen atoms is often considered in $\Delta G^H_{\text{ads}}$ to model coverage effects and the quantity is then normalized by the number of available surface sites, see also Sec. 2.2.4.

The importance of $\Delta G^H_{\text{ads}}$ for facile electrocatalysis is easily motivated since a surface adsorbed hydrogen atom is the key intermediary in both HER reaction mechanisms. According to Sabatier's principle, the strength of the bond between a catalyst and an intermediate should neither be too strong nor too weak: if the interaction is too strong (exergonic), the intermediate will poison the catalyst; if it is too weak (endergonic), the rate of intermediate binding to the surface is slow and limits the net reaction rate. A number of volcano plots have been created for HER catalysis on metal surfaces on the basis of this descriptor, or its experimental equivalents that measure the strength of the surface-hydrogen bond.\textsuperscript{8,37–41} Earlier experimental\textsuperscript{38} and theoretical\textsuperscript{8,37} studies indeed produced a volcano-shaped curve with an activity maximum near $\Delta G^H_{\text{ads}} \approx 0$ according to DFT calculations, which is the expected result if Sabatier's principle is the sole factor controlling reaction rate. However, a later study\textsuperscript{39} reexamined the computational volcano and revealed that the descending activity branch of the plot ($\Delta G^H_{\text{ads}} < 0$) disappears entirely once oxide-covered metals are removed from the data set. This observation can be rationalized by the presence of two distinct types of surface adsorbed hydrogens on the metals, namely, under- and overpotential deposited hydrogen. The former binds strongly to the surface and is typically the species considered in the descriptor model, while the latter binds more weakly and is likely the reactive hydrogen in HER.\textsuperscript{39,40} The exact role of these two hydrogen species still remains unclear, however, their presence enables the reaction to proceed through more favorable paths with higher energy intermediates, causing the disappearance of the descending activity branch.\textsuperscript{39}

Other deviations from Sabatier's principle were also discovered. The catalytic performance of Ag, Au, Cu were noted to be equivalent although hydrogen adsorption free energies on these metals vary by 0.4 eV, which lead the authors to deem the use of a single descriptor insufficient. The apparent contradiction was resolved by introducing the position of the metal $d$-electron band and its interactions with the proton $1s$ orbital as additional descriptor variables. In their refined model for HER catalysis, an active metal catalyst should fulfill...
three criteria: favorable binding of hydrogen to the surface ($\Delta G_{\text{ads}}^H \approx 0$), a $d$-band the spans the Fermi level, and strong long-range interactions of the $d$-band with the proton $1s$ orbital.\textsuperscript{42,43} The use of these electronic variables as descriptors is appealing from the perspective of electron transfer theories, pioneered by Marcus, Hush, Gerischer and many others, where analogous quantities enter into the rate expression for electron transfer, see e.g. Refs. 14,26,44,45 for overviews of this diverse field. The central concepts from electron transfer theories should generalize to electrocatalytic HER—a proton-coupled electron transfer (PCET) reaction—which might provide an additional research avenue in the future as will be briefly expanded upon in later sections.\textsuperscript{16,46–50}

It is not surprising, in hindsight, that the $\Delta G_{\text{ads}}^H$ descriptor founded on thermodynamic considerations is unable to capture all of the subtleties of the hydrogen evolution reaction, which exhibits complex kinetic phenomena.\textsuperscript{51} As already alluded to previously, another drawback of the descriptor-based model is the fact that the model relies on experimental measurements of catalytic activity. Fundamentally, such quantities are macroscopic in nature, that is, they measure the average performance of a material which arises as the sum of the structurally different regions that comprise the material. Because real catalysts, even single crystal electrodes, are rarely homogeneous, especially when exposed to electrochemical environments,\textsuperscript{52} the descriptor method is unable to directly pinpoint which surface site types contribute to enhanced catalytic activity and whose concentration should be maximized in an effort to further improve performance. This poses an issue that is particularly pronounced when heteroatom-doped or otherwise functionalized carbon nanotubes are used as catalysts because CNTs are notoriously heterogeneous. Specifically, experimental characterization techniques, such as X-ray and electron microscopies, can only identify the relative abundance of different types of dopants but are unable ascertain how exactly the atoms are arranged into the hexagonal atomic lattice.\textsuperscript{53} Although simulations admit the evaluation of $\Delta G_{\text{ads}}^H$ for any arrangement of atoms, it is not immediately clear, at least to the author, how simulated results can reliably be associated with experimental measures of catalytic activity. The matter is further complicated by difficulties in estimating the equilibrium hydrogen coverage of CNTs at electrochemical HER conditions, which is a fundamental ingredient of the descriptor-based model, see Sec. 2.2.4 for additional discussion.

Despite the issues highlighted in the discussion above, $\Delta G_{\text{ads}}^H$ calculations have been employed to study functionalization effects in carbon nanotubes, graphene, and other carbon-based materials, see e.g. recent reviews 4,5,11,54,55 and references therein. In these studies, the observed enhancement of catalytic performance due to functionalization is often directly rationalized in terms of a favorable adjustment of $\Delta G_{\text{ads}}^H$ when the modifications are introduced into the pristine material lattice, fully neglecting the stark disparities between experimental and simulated systems as well as other delicate issues related to creating a fully realistic computational model. However, as the Schmickler\textsuperscript{39,42,43} $d$-band model for metal-catalyzed HER revealed, a shift of $\Delta G_{\text{ads}}^H$ toward thermoneu-
trality does not necessarily correlate with enhanced catalytic activity because a multitude of other effects are also vital. This same trend is also readily apparent in the results for carbon-based materials: functionalizations with roughly similar values of $\Delta G_{\text{H ads}}$ to Pt have vastly different HER performance (see e.g. Fig. 5 in Ref. 55), which suggests that the simple $\Delta G_{\text{H ads}}$ descriptor is insufficient to explain trends arising from atomic-level structural modifications.

In the spirit of the $d$-band model for metals, $^{42,43,56}$ Qiao et al. $^{57}$ introduced an analogous orbital-based descriptor to assess the effects of heteroatom doping in graphene, formulated in terms of localized natural bond orbitals. This descriptor was used to measure the energy difference between the lowest valence orbital of the active site and the Fermi level of the graphene cluster. The analysis revealed that hydrogen adsorption free energies became more exergonic and approached $\Delta G_{\text{H ads}} \approx 0$ the deeper the valence orbital resided with respect to the Fermi level, which would imply a growth in HER activity if it could be safely assumed that thermoneutrality is the only necessary condition to maximize reaction rate. At first glance, this result appears to be at odds with observations on metals where a $d$-band spanning the Fermi level was a prerequisite for efficient catalysis; $^{43}$ however, the authors $^{58}$ later resolved the confusion by inspecting the highest peak of the active site density of states (DOS) and demonstrated that a shift of the DOS peak toward the Fermi level correlated with decreasing $\Delta G_{\text{H ads}}$. The use of an analogous metric to understand activity trends on CNTs was explored in Publication II and is detailed in Chap. 4.

By incorporating electronic effects, the model by Qiao et al. is an obvious improvement over the $\Delta G_{\text{H ads}}$ descriptor but it still relies on experiments to assign an activity ordering for different dopants, which is problematic in multiple regards as argued above. There is clearly a demand for direct simulations of reaction kinetics with atomic-level precision to advance the understanding of HER catalysis. This paradigm, dubbed kinetic modeling, will be briefly introduced next and contrasted to the descriptor method. A more thorough discussion of the challenges involved in this method will be given in Sec. 2.2.

The kinetic modeling method attempts to address the deficiencies discussed above by adopting a bottom-up approach where the catalytic performance of a material is assessed directly with reaction path sampling techniques. $^{8,22–24}$ Specifically, the HER activity of individual catalyst sites can be gauged by simulating the elementary reaction steps (2.1)-(2.3) that comprise the net reaction. In contrast to descriptor models, this method provides a means to identify kinetic barriers for HER in the form of activation (free) energies, in addition to revealing possible thermodynamic limitations. This approach has a number of key strengths. First, the method provides an unambiguous tool for comparing the performance of different catalysts and surface sites without requiring any experimental input, as long as the theoretical setup is kept consistent. Second, having uncovered that, e.g., introducing a certain dopant leads to an overall lower HER activation energy, the availability of the atomic-level reaction path and associated electronic structures provide a solid foundation for justifying the
origin of improved activity. These strengths demonstrate the prospective value that the simulation of reaction kinetics can add to electrocatalyst design as a complementary tool to experimental work, where resolution limitations hinder the interpretation of results on an atomic level.

Unfortunately, simulating reaction kinetics at an accurate level is far from trivial. To make the approach computationally tractable, the reaction conditions employed in actual experiments need to be simplified considerably, obfuscating direct quantitative comparison between simulations and experiments. Even then, the method demands orders of magnitude more computational resources than the descriptor-based method, which prohibits a large-scale screening of potential catalysts. Nonetheless, since the method should be able to correctly reproduce qualitative trends in electrocatalysis, in particular, the relative activity ordering of different surface sites, the approach was selected in this work to understand HER catalysis on functionalized carbon nanotubes at the atomic level. One of the primary research goals of this work was to develop a sufficiently comprehensive and reliable scheme for studying HER, which should also be transferable to other systems in addition to CNTs. The development of this model is described in-depth in Sec. 2.2.

Although the discussion thus far in this section has established a clear disparity between kinetic- and descriptor-based approaches to catalyst design, both in terms of ultimate goals and actual methodology, the approaches need not be mutually exclusive. For instance, Sang Hoon et al. first identified a set of potentially active sites for HER in 1-4 layer thick MoS2 nanoparticles using the $\Delta G_{\text{ads}}^\text{H}$ descriptor and subsequently performed kinetic simulations for the rate-determining step to exclude sites with slow kinetics. Recently, Exner and coworkers suggested a new strategy that convincingly attempts to bridge the gap not only between the two discussed computational approaches but also between simulations and experiments. In this method, experimental Tafel slope analysis on a single crystal surface is directly used to extract kinetic barriers along the reaction coordinate. Ancillary electronic structure calculations are then performed to evaluate the stabilities of different reaction intermediaries to complete a free energy diagram for the reaction. This framework defines a convenient tool for assessing the accuracy of simulated kinetic models of electrocatalysis in well-defined systems under mild approximations. Furthermore, the importance of entropic contributions can also be estimated, identifying the need to resort to computationally more demanding free energy sampling techniques.

### 2.2 Development of a Kinetic Model for Hydrogen Evolution

As was briefly mentioned in Sec. 2.1, the aim of the kinetic modeling approach is to compare different catalyst materials and active sites by characterizing the involved elementary reaction steps as accurately as possible. This is obviously a very demanding task due to the complexity of the electrochemical interface that
is formed at the boundary between the catalyst electrode and the electrolyte solution. An idealized description of this interface is sketched in Fig. 2.1.  

![Figure 2.1. Schematic illustration of the electrical double layer at the electrode-electrolyte interface.](image)

The electrode (gray spheres) is covered by a 0.7 monolayer of adsorbed hydrogen atoms (white). Under the assumed electrode conditions, anions (gold) are able to penetrate the solvation layer close to the electrode and adsorb specifically (nonelectrostatically) onto the surface, shedding a part of their hydration layer in the process (inner Helmholtz layer). By contrast, cations (blue) retain their solvation shell and cannot approach the electrode closer than the outer Helmholtz plane, marking the beginning of the diffuse layer. Ions in the diffuse layer interact with the electrode only through long-range electrostatic interactions. The nonzero surface charge of the electrode is screened by an excess of oppositely charged ions in the inner Helmholtz and diffuse layers. The drop of electric potential $\psi$ across the interface is depicted by the orange curve, saturating to a constant value $\psi_{\text{bulk}}$ in the bulk phase.

Examining Fig. 2.1, it is clear that the catalysis process is coupled to a number of other notable phenomena occurring at the interfacial boundary. These include the diffusion of reactants (products) to (away from) the electrode, the orientational and positional rearrangement of water molecules, the electrostatic interactions between reacting ions and counter and other ions, as well as structural and electronic alterations of the catalyst (corrosion, reconstruction, poisoning). Building a computational model that explicitly includes all of these phenomena at the same level of theory is far too demanding to simulate in practice. Instead, the model must be constructed in a way that is complex enough to capture the main features of the catalyst-solvent interface, while simultaneously maintaining a reasonable balance between computational cost and accuracy for the model to be applicable to multiple materials and surface sites.

The development of a kinetic HER model for carbon nanotubes is detailed in the remainder of this section. First, the concept of energy diagrams is introduced in Sec. 2.2.1, which serve as the concrete tool for measuring catalytic performance from simulations and facilitate comparisons of different catalysts and active surface sites. The selected algorithm for obtaining these diagrams is also outlined. Next, in Sec. 2.2.2, the proton reduction reaction (2.1) is described in terms of a band diagram model to motivate which aspects of the electrochemical
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interface from Fig. 2.1 are the most crucial to include in computational models of HER. Proposed methods for tackling the identified aspects are analyzed in Sections 2.2.3-2.2.5, where they are contrasted with the approaches employed in Publications I-II. The approximations introduced in this section are general in the sense that they are not limited to any specific electronic structure method, equally affecting wavefunction and density functional theory methods. Nevertheless, the following sections will almost exclusively focus on DFT-based strategies for modeling electrochemical reactions because DFT was adopted in practice to simulate the reactions on CNTs. Since using DFT involves introducing additional theoretical approximations, the inherent deficiencies of this methodology will also impact the accuracy of the kinetic HER model, which is a matter that will be further elaborated in Chapter 3.

2.2.1 Energy Diagrams as a Tool for Comparing Catalysts

The intricate structure of the electrode-electrolyte interface, illustrated in Fig. 2.1, poses a considerable challenge for the development of catalysis models at this interface. Focusing on HER catalysis in acidic media, the key reaction coordinate involves the diffusion of protons through the diffuse and Helmholtz layers to the interface boundary where the actual reduction reactions take place. The dynamic nature of this process could, in principle, be treated by combining molecular dynamics (MD) simulations with free energy sampling techniques, for instance, thermodynamic integration. Such simulations, however, would require long sampling periods due to the slow rearrangement of water molecules near interfaces, even in the absence of any other ions. This becomes a limiting factor for DFT-based simulations given the necessity for large systems and the complexity of the elementary reactions of HER (2.1)-(2.3).

To devise a computationally tractable catalysis model, it is worth noting that, in contrast to other ions, a solvated proton is highly mobile since it can diffuse from water to water via the Groththus mechanism. Moreover, the diffusion barrier of a proton through the solvent to the first interfacial layer should be roughly constant for same class materials under similar conditions (surface charge and potential, electrolyte composition) because the long-range structure of the electrochemical double layer is insensitive to the electrode material. This barrier should, in any event, be smaller than the barriers involved in the actual surface-catalyzed proton-coupled electron transfer steps. Primarily for these reasons, DFT-based MD simulations have at least thus far not been employed to simulate HER directly and using such methodology has been limited to simpler interface processes, such as salt dissociation.

Instead of considering the dynamics of the full system, it has become standard practice to assume that the necessary reacting species has already formed at the interfacial boundary for catalysis to proceed. Under this assumption, the task of characterizing the elementary steps of HER boils down to finding the minimum energy reaction path (MEP) that connects the fixed local energy
minima representing the reactant and product states of the reaction. The MEP conveys atomic-level information about the reaction mechanism, e.g., which atoms participate actively in the reaction and how they rearrange during the reaction. The MEP also defines the transition state of the reaction as the first-order saddle point along the path. This state is intimately linked to reaction kinetics. Indeed, according to harmonic transition state theory, the rate of a thermally activated reaction depends exponentially on the magnitude of the activation energy, \( E^\ddagger \), that is the energy of the transition state relative to the initial state (see below).

Although in practice most atoms far from the reaction center are kept frozen during an MEP calculation, entropic and zero-point vibrational effects can partly be included in this scheme by using vibrational normal mode analysis and tabulated thermodynamic information. The estimate for the barrier in a solvated system can be refined by considering multiple interfacial water structures as initial configurations.

Finding MEPS is a challenging optimization problem and a variety of algorithms have been proposed to tackle it. Following earlier studies of HER on platinum, the climbing image nudged elastic band (NEB) method was adopted in the current work, which has been illustrated in Fig. 2.2. In this method, the reaction path is described in terms of \( L \) discrete copies or “images” of the system, \( \{ R^K \}_{I=1}^L \), that are connected by harmonic springs, where \( R^K \) is a vector that contains the nuclear coordinates of all \( K \) atoms in the system. The reactant (initial) and product (final) states must be prepared carefully in advance to avoid introducing artificial bias into the results—a topic further discussed in Sec. 2.2.5. Initial guesses for the other images can be obtained, e.g., by a linear interpolation of the initial and final images, although using an educated guess.
for the transition state often accelerates convergence. The NEB algorithm then proceeds by minimizing the forces on the intermediary images subject to the constraint that the spacing between adjacent images is equal. This iterative optimization process is continued until the images lie on the MEP, determined by the numerical convergence of the band that connects the images. Concretely, the images are moved according to the force

$$
F_I (R^K_I) = F_I (R^K_I) || - F_I (R^K_I) \perp = k \left( |R^K_I - R^K_{I+1}| - |R^K_I - R^K_{I-1}| \right) \hat{t}_I - (\nabla E (R^K_I) - \nabla E (R^K_I) \cdot \hat{t}_I) \ (2.5)
$$

where the first term is the spring force acting parallel to the band with spring constant $k$, the last term is the true force arising from the potential energy landscape, $\nabla E (R^K_I)$, but with the component along the band projected out, and $\hat{t}_I$ is the local tangent at image $I$. To ensure rigorous convergence to a saddle point (the transition state), the force acting on the image highest in energy, $TS$, is modified so that it converges toward a global potential energy minimum in all directions except the MEP direction where it attains a maximum

$$
F_{TS} (R^K_{TS}) = -\nabla E (R^K_{TS}) + 2\nabla E (R^K_{TS}) \parallel \ (2.6)
$$

The MEPs obtained with NEB simulations are central to comparing different catalyst materials and active surface sites. Specifically, for multistep reactions such as HER, the reaction paths associated with each elementary reaction of the net reaction must first be computed. The activation, $E^\dagger$, and reaction, $\Delta E$, energies of these individual steps can then be extracted and combined to create reaction energy diagrams for the full mechanism. This process has been schematically illustrated in Fig. 2.3.

Reaction energy diagrams yield information about the prevalent reaction mechanism and they can be used for identifying the rate-determining step. Comparing the reaction energy diagrams for different catalysts or surface sites also allows the most active material and surface site to be recognized. Naturally, such comparisons are meaningful only if it can safely be assumed that the diagrams were obtained using comparable theoretical models and that the systems were prepared in analogous fashion, which are matters that will be further elaborated in the following Secs. 2.2.3-2.2.5. For instance, Fig. 2.3c suggests that site 1 would be more active toward HER than site 2 because the overall kinetic barrier determined by the Heyrovsky step is larger for the latter site, irrespective of the fact that the reaction is endothermic on site 1 and exothermic on the other. Here, it is worth noting that although the net energy change related to HER differs on the two considered sites, which at a cursory glance appears to violate fundamental thermodynamic concepts, the diagrams were constructed directly from NEB-modeled reaction states which obviously do not represent states in thermodynamic equilibrium. Furthermore, these diagrams include only potential energy contributions whereas entropic and other factors discussed in subsequent sections are fully ignored.
2.2.2 Electronic Description of Proton Reduction

The unique aspect that differentiates electrochemical and chemical surface catalysis is the fact that the rate of an electrochemical reaction can be controlled directly by varying the potential of the catalyst. In experiments, the catalyst or, more generally, the catalyst affixed to an electrically conductive support acts as the working electrode of an electrochemical cell. The working electrode is connected to a reference electrode through an external circuit. To highlight the challenges this innocuous-appearing experimental setup poses on computational modeling, a highly simplified band-diagram-based model for HER catalysis is presented in Fig. 2.4. 43

As Fig. 2.4 demonstrates, the number of electrons at the electrode is not a well-defined quantity because the electrode is free to exchange electrons with the reference electrode to maintain a constant electrode potential. On an absolute potential scale, the electrode potential, $U^\text{abs}$, is directly linked with the Fermi level of the electrode, $\mu$, through the relationship

$$U^\text{abs} = -\frac{\mu}{e} + \phi^S =: \frac{\Phi^S}{e}$$  \hspace{1cm} (2.7)

where $e$ is the elementary charge, $\phi^S$ is the Volta (outer) potential outside the solvent layer in vacuum, and $\Phi^S$ is the electrode work function, which is a
The electrode Fermi level, $\mu$, is fixed relative to a reference electrode through an external circuit. The number of electrons at the electrode is free to vary to maintain constant $\mu$. The metal is initially unable to reduce the proton to a hydrogen because the Fermi level resides below the proton 1$s$ orbital. This limitation is lifted by applying a cathodic (negative) overpotential, $\eta$, causing the Fermi level to shift above the 1$s$ state. Only the occupations of the electrode states are affected by the applied overpotential. A measure of the work required to transport an electron from the Fermi level to vacuum through the solvent, see Sec. 2.2.3 for further elaboration. The Fermi level is defined as the electron energy level which has a 50% probability of being occupied at thermodynamic equilibrium at temperature $T$. The Fermi-Dirac distribution function provides a rigorous definition for the Fermi level

$$f(\epsilon_i) = \frac{1}{1 + \exp \left( (\epsilon_i - \mu) / k_B T \right)}$$  \hspace{1cm} (2.8)$$

where $k_B$ is the Boltzmann constant and $\epsilon_i$ is the energy of the electron single-particle state $i$. As a note regarding notation, the formally more correct term here would be the electrochemical potential of electrons in the electrode and not the Fermi level, but these terms are used synonymously throughout this thesis, which is a valid approximation for systems at room temperature.

The band diagram in Fig. 2.4 also rationalizes how the rate of HER is linked to the electrode potential. Initially, under no applied bias $U = U^*$, the reaction rate is virtually nonexistent because the Fermi level lies beneath the proton 1$s$ state, effectively preventing the electrode from reducing the proton. A drastic increase in the measured current density $j$ will eventually be observed once a sufficiently large cathodic overpotential, $\eta$, is applied to shift the position of the Fermi level. This threshold value is defined as the onset potential for HER. Further increasing the overpotential will accelerate the reaction rate as more states in the conduction band become available for reducing the proton. Note that the actual reaction rate depends on other factors in addition to the energy.
level alignment, for instance, the electronic coupling between the electrode frontier orbitals and the proton 1s state, which is proportional to the orbital overlap.\textsuperscript{26,43,44} The delicate interplay between the electrode Fermi level and the proton 1s state suggests that the relative positions of these quantities at zero applied bias is a key catalyst design criterion. More concretely, an ideal catalyst should require only a small overpotential for the onset of HER catalysis, which is a combination of the band alignment and other electronic factors as discussed above. The concepts presented herein for the Volmer step can be generalized to the Heyrovsky step.\textsuperscript{43}

Altering the electrode potential has secondary effects on the structure of the electrode-electrolyte interface influencing, e.g., the surface conditions at the electrode and the orientation of interfacial water molecules, which further complicates the task of devising a computational HER model.\textsuperscript{77} In the following Sections 2.2.3-2.2.5, the approaches taken in Publications I-II to tackle HER catalysis on carbon nanotubes are contrasted to procedures adopted elsewhere in the literature, mainly, to describe metal-water interfaces. The analysis is broken down to separate discussions on direct electrode potential effects on catalytic performance (Sec. 2.2.3) and indirect effects on the electrode hydrogen coverage (Sec. 2.2.4) and the interfacial electrolyte (Sec. 2.2.5).

### 2.2.3 Electrode Potential

Because the electrode Fermi level is fixed in experimental measurements, this suggests that the relevant thermodynamic ensemble for modeling the system is the electronic grand canonical $\mu VT$ ensemble, where the corresponding energy measure is the electronic grand potential, or the Landau (free) energy, $\Omega = E + \mu N_e$, where $N_e$ is the number of electrons in the system. Conventional electronic structure software, by contrast, have been developed for simulations with a constant number of electrons in the microcanonical ensemble $N_e V E$.

From a theoretical perspective, there is no fundamental obstacle for performing variational grand canonical simulations;\textsuperscript{78,79} however, in practice, converging such calculations has proven difficult with existing algorithms.\textsuperscript{80} Despite promising algorithmic developments reported recently by using a computational potentiostat\textsuperscript{81-83}—a reservoir of electrons implemented similarly to a thermostat—or by performing the simulations in the framework of joint density functional theory,\textsuperscript{84} the prevalent strategy for treating electrochemical systems has been to approximate grand canonical behavior from constant charge simulations.

The discrepancies between experimental and computational setups have two primary consequences for modeling electrochemical reactions. First, the electrode potential in simulations cannot readily be controlled, although indirect methods can be adopted as will be demonstrated below. Second, during an electrochemical reaction, the Fermi level will shift as the electrode loses or gains electrons over the course of the reaction. The magnitude of this shift is usually substantial, at least several hundred mV, which is unreasonably large from
Figure 2.5. Determination of the absolute electrode potential from the averaged electrostatic potential for a solvated nanotube electrode at charge neutral conditions ($q = 0$). The electrode potential, $U_{\text{abs}}$, is related to the Fermi level, $\mu$, the vacuum potential, $\phi_S$, and the work function, $\Phi_S$, through Eq. (2.7). Once the electrode is charged by adding electrons to the system, the compensating background charge density prevents the determination of the vacuum potential. An alignment scheme, $\Delta \phi_{\text{water}}^{q}$, is employed to approximate the absolute potential, $U_{q}^{\text{abs}}$, of the charged electrode.

an experimental vantage point. The latter effect will naturally vanish as the system size tends to infinity, which, in fact, forms the basis for a method where reaction kinetics are corrected to constant potential by repeating calculations with multiple system sizes and extrapolating the results to infinite size.\textsuperscript{64,65}

The electrode Fermi level and, through Eq. (2.7), the absolute electrode potential are both well-defined observables in charge neutral electronic structure simulations. Concretely, the electrode potential can be evaluated by averaging the total electrostatic potential (the Hartree potential) felt by the electrons in the direction of the electrode surface normal vector. This process has been conceptually visualized in Fig. 2.5 for a solvated carbon nanotube electrode.

Although the electrode potential cannot be controlled directly in microcanonical simulations, the number of electrons at the electrode can be altered with various schemes, which will also induce a change in the potential as a consequence. The simplest scheme involves adding or removing electrons from the system giving the system a net charge. Because the electrode Fermi level resides in the band gap of liquid water, or at least should in the absence of DFT errors (see Chapter 3),\textsuperscript{13,77} the added electrons will mostly localize on electronic states that can be associated with the electrode. Unfortunately, to avoid divergence of the electrostatic energy in periodic systems, the added charge must be compensated by introducing a counter charge with opposite sign to the system, e.g., a uniform background density implicitly added by electrostatics solvers subject to periodic boundary conditions.\textsuperscript{85} This obfuscates the determination of the vacuum potential, $\phi_S$, and the absolute electrode potential since the system will no longer contain a field-free vacuum region, see Fig. 2.5. An added complication arises due to spurious electrostatic interactions between the electronic system and the background charge, which however diminish with increasing system volume and are partially screened by the solvent and the electrode.

Given the aforementioned difficulties with the homogeneous background
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charge, a number of alternative strategies for compensating the added charge have been proposed which include: introducing explicit counter ions,\cite{86} localizing the background density to a specific region of the system,\cite{6,78,79,87–89} or incorporating the charge in continuum solvation schemes by adapting Poisson-Boltzmann theory.\cite{23,90–93} The listed methods, at least partially, address the issues related to spurious interactions with the background charge, yet it is not always straightforward to determine the absolute electrode potential with them either. Moreover, using these approaches introduces a host of new challenges, but a detailed discussion of these matters is beyond the scope of this thesis.

The possibility of indirectly controlling the electrode potential by adding or removing electrons from the system suggests that microcanonical simulations can be used to approximate grand canonical behavior. Concretely, the most rigorous method would be to introduce a separate self-consistency loop to electronic structure codes, where the number of electrons is reoptimized during each step of, e.g., a reaction barrier simulation in order to fix the Fermi level to the desired target value.\cite{89,92} This algorithm will obviously impose an increase in computational cost compared to constant charge simulations, and it will also require a correction to calculated electronic energies in order to compare energy differences in systems with a varying number of electrons. In a very recent methodological development, these issues were addressed by combining implicit solvation and a jellium model, which enabled the calculation of potential-dependent HER kinetics on pristine Pt(111) with a well-defined absolute potential reference.\cite{89}

A computationally cheaper, though less rigorous, method to approximate constant Fermi level simulations is to apply a correction to microcanonical electronic structure calculations a posteriori. An example of such a method is the previously mentioned approach where extrapolation to infinite system size was leveraged to obtain constant potential energetics.\cite{64,65} In this scheme, the electrode potential is controlled in discrete amounts by adding extra hydrogens to the interfacial water layer, which spontaneously donate their electron to the electrode and form protons, thus maintaining overall charge neutrality. Nørskov and Chan\cite{94,95} recently suggested that the extrapolation to infinite system size is unnecessary and that a correction to constant potential energetics can be derived directly from one constant charge simulation, establishing a roughly one-to-one correspondence between results obtained with both schemes.

In a different approach, the so-called double reference method,\cite{96,97} simulations are performed in charged supercells and the charged system Fermi level, $\mu_q$, is related to the well-defined neutral system vacuum potential, $\phi^S$, using two internal potential references. The method by Sprik et al.\cite{75,98,99} suggests an appealing alternative for determining the electrode potential of charged systems, where the issue of aligning the charged system Fermi level to a vacuum potential is avoided altogether by relating it to the free energy of reversible electron and proton injection. A modified double reference scheme was adopted in Publication I to estimate electrode potential effects in HER catalysis on CNTs. In contrast to the original model, only a single reference plane was defined at the electrostatic...
potential minimum corresponding to the first solvent layer, as shown in Fig. 2.5. The charged system absolute potentials were then approximated by

$$U_{q}^{\text{abs}} = -\frac{\mu_q}{e} + \phi^S + \Delta\phi_{\text{water}}$$  \hspace{1cm} (2.9)

A continuous mapping from microcanonical, $E$, to grand canonical energies, $\Omega$, was established by adopting a capacitor model like in the original method.$^{96,97}$

As the discussion in this section has revealed, a vast number of methods are available to include the effects of electrode potential in electronic structure calculations. No consensus on which methods should be preferentially employed to tackle the electrode potential problem has thus far emerged. A lack of systematic method benchmarking has exacerbated this issue, though one might argue that some methods are theoretically more justified than others. This thesis does not attempt to resolve this complicated matter either and will settle on analyzing the accuracy of the modified double reference scheme in Chap. 4.

Before concluding this section, I wish to introduce one final method in addition to the approaches already highlighted above. This so-called computational hydrogen electrode$^{100}$ (CHE) or thermochemical method is conceptually simple and has become widely adopted not only in the studies of HER but also, e.g., in the studies of $\text{CO}_2$ reduction$^{101–103}$ and other electrochemical reactions. As the latter name suggests, the CHE method differs from other schemes discussed in this section since reaction kinetics are fully neglected and only the relative thermodynamic stabilities of different reaction intermediaries are considered. Janik and coworkers$^{104}$ have later suggested an extension to the CHE model where the potential dependence of activation energies for certain types of reactions can be evaluated by considering the nonelectrochemical analogue of the reaction and by leveraging Marcus theory. Alternative transfer-coefficient-based strategies have also been proposed.$^{105,106}$ The original CHE method resembles the descriptor-based method$^{37}$ discussed earlier in Sec. 2.1; however, the CHE method is, in many respects, an improvement over the latter because all intermediary configurations along a reaction path are modeled in the method, while typically only a single variable is considered in the descriptor method. Furthermore, the effects of electrode potential are included in the CHE scheme by linearly shifting the energies of reaction steps which involve the concerted transfer of a proton and an electron.$^{100}$ The key assumption of this a posteriori correction is that the proton and electron are in thermodynamic equilibrium with molecular hydrogen $\text{H}_2$ at standard conditions ($T = 298$ K, $p_{\text{H}_2} = 1$ bar, $\text{pH} = 0$), which defines the $U = 0$ V potential in the standard hydrogen electrode (SHE) scale. In essence, using this scheme allows one to replace all chemical potential terms involving $\text{H}^+ + e^-$ with the chemical potential of $\text{H}_2$ plus a potential shift term $-eU$. As a concrete example of the CHE approach, the potential-dependent Volmer step (2.1) reaction free energy can be expressed as

$$\Delta G_{\text{Volmer}} (U^{\text{CHE}}) = G_{\text{H}^*} - G_* - \frac{1}{2} G_{\text{H}_2(g)} - eU$$  \hspace{1cm} (2.10)
2.2.4 Hydrogen Coverage

A key prerequisite for inner sphere electron transfer reactions on electrodes, as exemplified by HER, is a strong interaction between the electrode and the reactant or product, often manifesting as the specific adsorption of these species or a reaction intermediate on the electrode surface.\(^{26}\) Looking back at the elementary steps of hydrogen evolution (2.1)-(2.3), it is evident that atomic hydrogen is the relevant adsorbent for HER in acidic conditions, formed through the reduction of protons via the Volmer step. The surface hydrogen coverage, \(\theta\), is a fundamental parameter that governs HER catalysis because the net rate of molecular hydrogen production is proportional to \(\theta\), irrespective of the actual reaction mechanism. The hydrogen coverage is defined as the ratio of hydrogen blocked and free surface sites: \(\theta = n/N \in [0,1]\) where \(n\) and \(N\) are the number of adsorbed hydrogens and surface sites, respectively. Other species may also specifically adsorb on the electrode under electrochemical reaction conditions. Depending on species, the adsorption may either be beneficial (coadsorption) or disadvantageous (competing reactions, surface poisoning) to HER but their explicit impact on catalytic performance is ignored throughout this section.

The effects of hydrogen coverage on the rate of HER can be understood with a simple analysis based on Butler-Volmer kinetics, which enables the derivation of a relationship between the observed current, \(j\), and the overpotential, \(\eta\).\(^{26}\) To that end, let \(v_X^{\text{red}}, v_X^{\text{ox}}\) denote the rates of the forward (reduction) and backward (oxidation) reactions of elementary step \(X\) with associated rate constants \(k_X^{\text{red,ox}}\).

Without loss of generality, the subsequent analysis will focus on the Volmer-Heyrovsky mechanism. A significantly more comprehensive kinetic analysis is presented in Ref. 107 where the authors also discuss the challenges of interpreting experimental kinetic measurements. Under steady state conditions and assuming that the Heyrovsky step is irreversible, \(d\theta/dt = v_{\text{Volmer}}^{\text{red}} - v_{\text{Volmer}}^{\text{ox}} - v_{\text{Heyrovsky}}^{\text{red}} = 0\), the surface hydrogen coverage can be shown to obey

\[
\theta = \frac{k_{\text{Volmer}}^{\circ} [H^+]}{(k_{\text{Volmer}}^{\circ} + k_{\text{Heyrovsky}}^{\circ}) [H^+] + k_{\text{Volmer}}^{\circ} \exp(-f \eta)}
\]

while the observed current is

\[
j = 2F v_{\text{Heyrovsky}}^{\text{red}} = 2F k_{\text{red}}^{\circ} [H^+] \theta \exp((\alpha - 1)f \eta)
\]

where \(k_X^{\circ}\) is the equilibrium rate constant of step \(X\) at \(\eta = 0\), \(\alpha\) is the charge transfer coefficient, \([H^+]\) is the (surface) concentration of the proton, and \(f\) denotes the reduced Faraday constant \(f = F/RT\). Eq. (2.11) shows that the coverage not only depends on the relative rates of the Volmer and Heyrovsky steps but also on the electrode potential through the exponential overpotential term. Two limiting cases \(\theta \approx 0\) and \(\theta \approx 1\) can be identified from this equation (note that \(\eta < 0\), which indicate that there are either virtually no adsorbed
hydrogens on the electrode or that the electrode is fully saturated, respectively. The former case is observed when the rate of the reverse Volmer reaction (electrochemical desorption of hydrogen) is significantly faster than the forward Volmer-Heyrovsky mechanism, \( k_{\text{Volmer}}^{\text{ox}} \gg k_{\text{red}}^{\text{Volmer}}, k_{\text{red}}^{\text{Heyrovsky}} \). The opposite limit is reached when the Volmer reaction is notably faster than the other reactions, \( k_{\text{red}}^{\text{Volmer}} \gg k_{\text{ox}}^{\text{Volmer}}, k_{\text{red}}^{\text{Heyrovsky}} \). Intermediate values of \( \theta \) are observed when the rates of all reactions are comparable or with intermediate overpotentials.

The simple analysis above demonstrated that there is an intimate connection between the rate of HER catalysis and the surface hydrogen coverage. In order to develop a realistic computational model for HER, it is therefore paramount to include the effects of hydrogen coverage. The immediate next question is how should the hydrogen coverage be computed. Looking at Eq. (2.11), this task appears daunting because even calculating the steady-state coverage for a fixed mechanism requires knowledge of the kinetic rates of all the elementary steps, including explicit entropic contributions. In general, the reaction rate constants calculated for a specific surface site will depend on both the global and microscopic (local) hydrogen coverages, and their potential dependence might exhibit deviations from the exponential Butler-Volmer relationship. A precise microkinetic model for HER could be derived using kinetic Monte Carlo if all the rate constants could somehow be determined, but even under simplifying assumptions, this strategy is far too costly to utilize in practice.

A more approximate model to evaluate the hydrogen coverage is evidently needed to circumvent the prohibitive cost of the direct method. A straightforward simplification involves neglecting the kinetics of the process and focusing solely on the thermodynamics. Moreover, the CHE method presented earlier suggests that instead of explicitly considering hydrogen adsorption via the reduction of a proton (Volmer reaction), it is possible to estimate the coverage from the dissociative adsorption of molecular hydrogen, \( \frac{1}{2} \text{H}_2(\text{g}) + * \rightarrow \text{H}^* \). This also simplifies the inclusion of electrode potential effects which now amount to a mere linear shift of calculated adsorption energies. Within this scheme, the equilibrium hydrogen coverage \( \theta_{\text{eq}}(U) \) at a given electrode potential \( U \) can be solved by incrementally adding hydrogens to the surface and by evaluating the value of the differential adsorption free energy

\[
\Delta G_{\text{diff}}(\theta, U) = G_{n\text{H}^*} - G_{(n-1)\text{H}^*} - \frac{1}{2} G_{\text{H}_2(\text{g})} - eU \tag{2.13}
\]

until the equilibrium coverage defined by \( \Delta G_{\text{diff}} = 0 \) is reached. This scheme has been shown to reproduce the experimental equilibrium coverages of underpotential deposited hydrogen on pristine Pt(111), Pt(110) and Pt(100) crystal facets at \( U = 0 \) V vs. SHE rather accurately, despite the fact that solvation and other aspects of the electrochemical double layer are typically fully neglected. An obvious complication arises when considering nonideal electrode surfaces that contain steps, kinks, grain boundaries, and other defects because the number of permutations the \( n \) hydrogen atoms can be arranged into at a particular
coverage rapidly start increasing as the surface becomes more heterogeneous. Indeed, for any given discrete $\theta$, a large number of geometry optimization simulations will be needed to identify the hydrogen configuration with smallest free energy. This factor does not pose an issue for pristine crystal facets as symmetry considerations greatly reduce the total number of permutations.

Determining an equilibrium hydrogen coverage for carbon nanotube electrodes, even for a pristine unmodified CNT, is in many respects more challenging than on low index metal facets. First of all, no experimental reference data is available to corroborate computational results, which is natural given the limited ability to control the purity of the nanotubes and the issues of determining what is the actual arrangement of atoms in the CNT. Moreover, it was discovered in Publications I-II that CNT surface sites exhibit strong neighbor-neighbor interactions toward hydrogen adsorption. In brief, both repulsive (increasing $\Delta G_{\text{diff}}$) and attractive effects were observed that extend over multiple adjacent surface sites, stemming from disruptions of the CNT $\pi$-bond network, see Chapter 4 for the specific details. These effects were also shown to influence catalytic activity. Instead of attempting to estimate an equilibrium hydrogen coverage for CNTs with the CHE approach, the following strategy was adopted in order to properly include the effects of coverage on reactivity. For a selected surface site, a sequence of hydrogen adsorption energy calculations was performed by varying the local hydrogen coverage around the active site. Representative configurations with high, intermediate (zero coverage) and low hydrogen adsorption energies were then selected for subsequent NEB-based reaction path simulations. Finally, linear dependencies between HER activation and reaction energies on $\theta$ were derived by fitting. The quality of this model is discussed in Chapter 4.

2.2.5 Interfacial Electrolyte Structure

The structure of the electrochemical interface and the catalytic properties of the electrode depend on the nature of the electrolyte solution in contact with the surface. Comprehensive studies of platinum surfaces have revealed that these effects are generally quite complex. Changing the solution pH has the most profound effect on HER activity, resulting in a two order of magnitude decrease in the measured standard exchange current density when pH is increased from 0 to 13 (see e.g. Ref. 110). The formation of the underpotential deposited hydrogen layer is also sensitive to pH conditions. A pH-dependent anomalous shift of the peak potential associated with hydrogen adsorption can be observed for Pt(110) and Pt(100) surfaces but not for Pt(111). The origins of this phenomenon remain unknown although different explanations based on water reorientation effects, coadsorption of alkali cations, replacement of adsorbed H with O and OH species, and the pH dependence of (apparent) hydrogen adsorption energies have been suggested. Adsorption of counter anions is another feature affecting hydrogen adsorption behavior, however, minimal effects on HER activity have been reported when using different acids ($\text{H}_2\text{SO}_4$ vs. $\text{H}_2\text{ClO}_4$).
in the relevant potential region at low pH values.\textsuperscript{110,113} Surprisingly, a slight sensitivity of HER performance to the presence of different alkali cations has been reported, despite conventional double layer models (Fig. 2.1) suggesting that these ions are not specifically adsorbed.\textsuperscript{115}

Capturing pH effects in electronic structure simulations is challenging much for the same reasons as was discussed earlier in relation to the electrode potential, namely, the traditional methodology is incompatible with open boundary conditions.\textsuperscript{7} More concretely, once a proton is consumed in a reaction, say the Volmer reaction (2.1), the electrolyte pH will shift toward higher values due to finite size effects because constant pH, or more rigorously a constant proton chemical potential, is not maintained by an external reservoir of protons. Computational approaches toward realizing constant pH simulations have been proposed in the biochemistry community, see e.g. Ref. 116 and references therein, but a survey of such methods is beyond the scope of the present work. Here, it is crucial to note that proton transfer is always coupled to electron transfer which suggests alternative approaches can be explored. Independently of each other and using distinct methods, Rossmeisl and coworkers\textsuperscript{117,118} as well as Sprik et al.\textsuperscript{75,98,99} have pioneered efforts to include pH effects in proton-coupled electron transfer reactions. The methods proposed by the former group are intimately linked to electrode potential effects and warrant a brief conceptual introduction.

Starting from the same fundamental premise as the computational hydrogen electrode, but by distinguishing the contributions due to pH and electrode potential, an extrapolation scheme was devised which allows the evaluation of free energies for interfacial structures as the function of pH and electrode potential.\textsuperscript{117} This scheme is an extension to the constant potential method where explicit hydrogens are added or subtracted to control potential.\textsuperscript{64,65} Within this framework, the explicit equation for evaluating the energy of an interfacial system with workfunction $\Phi^S$ and $n \in \mathbb{Z}$ added/subtracted hydrogens is given by

$$E(n, \Phi^S, \text{pH}) = E(n, \Phi^S) - E(n = 0) - \frac{n}{2} E_{H_{2(g)}} - n (\Phi_{\text{SHE}} - \Phi^S - 2.303 k_B T \cdot \text{pH})$$ \hspace{1cm} (2.14)$$

where $E(n = 0)$ is the electronic energy of the system without extra hydrogens and $\Phi_{\text{SHE}}$ is the work function at pH = 0 and $U = 0$ V vs. SHE.\textsuperscript{117} The method was later combined with molecular dynamics simulations and Metropolis Monte Carlo annealing to evaluate observables as ensemble averages of the grand partition function.\textsuperscript{118} Despite elucidating how interfacial water rearranges due to potential and pH changes, thus far, no attempts to probe the pH dependency of reaction paths have been reported with this generalized CHE method.\textsuperscript{118–120} Given the faster kinetics of HER in acidic conditions, pH $\approx 0$, the scope of this thesis was narrowed down to the appropriate reaction mechanisms and, following the usual convention in the field,\textsuperscript{8} the effects of varying pH have been ignored throughout. A major computational hurdle related to kinetic reaction modeling remains even at fixed pH conditions, namely, how to properly describe
the structure of the interfacial water and the solvated proton. The formation of the electrochemical interface is governed by the interplay of various mutually dependent factors: electrode potential, surface hydrogen coverage, catalyst properties such as hydrophobicity and roughness, the presence of specifically and unspecifically adsorbed nonreactive ions, to name just a few factors. The inherent complexity of the interface suggests that, ultimately, a static representation of the interface as typically adopted in kinetic catalysis studies is inadequate to capture all intricacies of HER in full quantitative accuracy. However, as the primary goal here is to gain insight into catalytic trends between different surface sites on carbon nanotubes, it should be a perfectly valid assumption to decouple these factors, i.e., to employ a fixed representative interfacial structure to probe kinetic effects on different surface sites.

In computational electrocatalysis studies, the most common approach to represent the electrode-electrolyte interface has been to include 1-4 layers of frozen ice-like water on top of the electrode, annealed to a local energy minimum configuration that is dependent on the hydrogen coverage and other factors. The roots of this approximation can be understood to stem from early experimental attempts to quantify the metal-water interface in ultrahigh vacuum (UHV) conditions, which suggested that the first interface layer adopts a uniform bilayer structure composed of water hexamers, seeking to maximize surface-water and water-water interactions. Modern UHV experiments and simulations have largely disproven this model as too simple by demonstrating that on most surfaces the interface is more diverse and disordered, exhibiting structurally more complex motifs as well as dissociated water molecules. Characterizing the structure of interfacial water at ambient electrochemical conditions, where thermal fluctuations, electrode potential, and other contributions influence water ordering, is challenging due to the unavailability of direct experimental tools to probe the interface. Regardless, the aforementioned factors are expected to decrease water ordering in the first interfacial layers in comparison to UHV conditions, although these molecules cannot be defined as fully liquid-like either. The effects of specifically adsorbed ions have largely been ignored apart from notable exceptions where the coadsorption of hydrogen (or hydroxide) and alkali cations has been modeled using an extended CHE method. This will also be the working assumption in the present work as the aim is to gain an initial understanding of HER catalysis on carbon nanotubes.

Pristine carbon-based materials, such as graphene, are known to be very hydrophobic, i.e., they exhibit low friction for water diffusion due to weak mutual interactions, although water molecules in the first interface layer do adopt a preferential orientation with the dipole moment vector aligned roughly tangentially to the surface. The use of an ordered ice-like description of interfacial water with the first layer oriented oxygen down, as discussed above, is therefore clearly not a suitable representation of the CNT-water interface, where the curvature of the nanotube introduces a further factor. Prior computational studies of HER kinetics on CNTs have not extensively considered solvation effects: they have
either been ignored altogether or included via a simplified water droplet model, where few to tens of molecules are added around the active proton species.\textsuperscript{9,10} To validate the accuracy of the employed electronic structure method (see also Chap. 3),\textsuperscript{13,77} a molecular dynamics simulation with several hundred water molecules was used in Publication I to generate a static CNT-water interface for subsequent kinetic simulations. An obvious, though computationally very costly, path toward more comprehensive HER kinetics would involve sampling a larger number of initial solvent configurations with different water orientations both globally around the whole CNT and locally around the active site. The computationally cheaper droplet model was adopted in conjunction with open-ended CNTs in Publication II since notably more active sites were investigated in this study. Combining the droplet model with polarizable continuum solvation models or electrochemistry-motivated Poisson-Boltzmann models,\textsuperscript{93} which include double layer ion effects in a mean-field manner, could lead to accuracy improvements but these possibilities were not investigated herein.

The accurate representation of the solvated proton species that reacts in the Volmer (2.1) and Heyrovsky (2.2) steps is intimately linked with the proper depiction of interfacial water. As discussed earlier in Sec. 2.2.1, a solvated proton, described conventionally as the hydronium cation H\textsubscript{3}O\textsuperscript{+}, readilydiffuses between water molecules via the hydrogen bond network. A number of idealized cluster structures have been proposed to describe the diffusion process where the normal hydrogen bond structure of water is disrupted by the formation of configurations with several water molecules actively participating in the hydration of the proton.\textsuperscript{63} The simplest structures are the so-called Zundel [H\textsubscript{2}O\cdots H\cdots OH\textsubscript{2}]\textsuperscript{+} (H\textsubscript{5}O\textsubscript{2}\textsuperscript{+}) and Eigen H\textsubscript{9}O\textsubscript{4}\textsuperscript{+} cations.

It remains unclear how the usage of these different species affects kinetic studies of HER. The proton has predominantly been modeled as a hydronium cation in prior studies, created by adding an extra hydrogen to an interfacial water molecule and oriented toward the catalyst surface. All other water molecules in the system apart from H\textsubscript{3}O\textsuperscript{+} are typically frozen to their reactant state configuration during actual NEB reaction path simulations.\textsuperscript{8,65} The proton will tend to spontaneously diffuse toward the bulk water when placed directly at the interface, at least on CNTs. In order to account for this behavior in a computationally affordable manner, the solvated proton was described as a Zundel cation in Publications I-II, again preventing all other water molecules from moving during HER NEB simulations. Finally, it is worth noting that especially when a droplet solvation model is adopted, special attention must be paid to the creation of the solvated proton species as the kinetic results can inadvertently be biased by placing the cation too close to the active catalyst site. This issue was avoided in Publication II by tuning the Zundel-active site distance so that it was in line with the observed values in the fully solvated system in Publication I.
3. Density Functional Theory

The quantum state of a many-electron system is represented by the abstract complex vector $|\Psi\rangle$, a ket in the bra-ket formulation of quantum mechanics pioneered by Dirac.\textsuperscript{130} The ket formally belongs to a vector space endowed with an inner product, the so-called Hilbert space, although in practice only the position, $r$, or position-spin, $(r, \sigma)$, bases of this vector are necessary herein. Under the Born-Oppenheimer approximation allowing the separation of nuclear and electronic degrees of freedom, the electronic wavefunction of a system with $N$ electrons, $\Psi(r, r_1, ..., r_{N-1})$, can be defined as the projection of $|\Psi\rangle$ onto the position basis $\Psi(r, r_1, ..., r_{N-1}) := 〈r, r_1, ..., r_{N-1} | \Psi\rangle$.

The physical properties of a system of electrons are fully determined by the wavefunction. They can be measured as observables of suitable linear operators. The arguably most important operator is the Hamiltonian operator, $\hat{H}$, which measures the total energy of a system and describes how electrons interact with each other and the environment. The Hamiltonian can be defined as the sum of kinetic, external potential (electron-nuclei and other contributions) and electron-electron operators $\hat{H} = \hat{T} + \hat{V} + \hat{W}$, ignoring contributions from relativistic effects and external magnetic fields. The time-independent Schrödinger equation

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$

defines the fundamental relation between the Hamiltonian and the wavefunction, where the standard abuse of notation $\hat{H} |\Psi\rangle \equiv 〈r, r_1, ..., r_{N-1} | \hat{H} |\Psi\rangle$ has been employed. The Schrödinger equation implies that $\{ |\Psi_i\rangle, E_i \}_{i \in \mathbb{N}}$ are eigenpairs of the Hamiltonian with indices $i > 0$ corresponding to excited states. The variational principle states that the ground state wavefunction $|\Psi_0\rangle$ with energy $E_0$ can be found by minimizing the energy with respect to the wavefunction\textsuperscript{131}

$$E_0 = \min_{\Psi} E[\Psi] = \min_{\Psi} \frac{〈\Psi | \hat{H} |\Psi\rangle}{〈\Psi |\Psi\rangle}$$ \hspace{1cm} (3.2)

Above, the term in the numerator is the expectation value of the total energy operator, the denominator ensures normalization, and $〈\Psi |$ is the dual of $|\Psi\rangle$, that is, a bra vector $〈\Psi | := |\Psi\rangle^\dagger$. Using the variational principle (3.2) to solve the wavefunction of an $N$-electron system is complicated by the fact that electron
correlation effects couple all the degrees of freedom, which places a limit on
the system sizes that are computationally feasible to simulate with an exact
treatment. This limitation can be resolved by switching to more approximative
electronic structure methods that represent $|\Psi\rangle$ in a simpler form. Broadly
speaking, these methods can be divided into two main classes. The first class
contains molecular-orbital-based wavefunction approaches, such as the Hartree-
Fock method, which attempt to construct increasingly accurate estimates of the
true wavefunction as linear combinations of simpler, idealized wavefunctions.
The latter class is comprised of density functional methods that forego the
actual treatment of $|\Psi\rangle$ and instead attempt to minimize the electronic energy
directly by varying the electron density. DFT approaches can be further divided
into hierarchical categories in order of increasing accuracy and computational
complexity. Although the simplest DFT approximations are rarely as accurate as
the best wavefunction methods, they are far superior in terms of computational
efficiency and are the only viable method to treat the system sizes needed in
electrocatalysis applications.

The remainder of this chapter is divided as follows. First, in Sec. 3.1, a brief
overview of the theoretical foundations of DFT will be presented. The actual
algorithms adopted in this thesis to perform DFT simulations will then be high-
lighted in Sec. 3.2. The fundamental deficiencies of DFT and their implications
on the constructed HER catalysis models are subsequently discussed in Section
3.3. Finally, a method to estimate these errors and to simulate various electron
transfer processes will be introduced in Sec. 3.4.

### 3.1 Fundamentals of Kohn-Sham Density Functional Theory

Hohenberg and Kohn\textsuperscript{132} established the foundations of DFT by demonstrating
that the ground state wavefunction $|\Psi\rangle$ of a system is a unique functional of the
ground state electron density $\rho(r)$, that is, the wavefunction is fully determined
by the density, up to an inconsequential phase factor

$$|\Psi\rangle = |\Psi[\rho]\rangle$$

where the 0 subscripts denoting the ground state have been dropped for
brevity. The derivation and proof of this result is standard textbook material and
will consequently be omitted.\textsuperscript{133} The main implication of the Hohenberg-Kohn
theorem is that the measurable properties of a system, which were operator
observables of the wavefunction, are also functionals of the electron density.
This, in particular, holds for the total energy that can now be expressed as

$$E[\rho] = \langle \Psi[\rho] | \hat{H} | \Psi[\rho] \rangle = \langle \Psi[\rho] | \hat{T} + \hat{W} | \Psi[\rho] \rangle + \int v(r)\rho(r)dr =: T[\rho] + W[\rho] + V[\rho] =: F[\rho] + V[\rho] \tag{3.4}$$
where the electron density $\rho(\mathbf{r})$ is defined as the observable of $\hat{\rho}$:

$$
\rho(\mathbf{r}) = \langle \Psi | \hat{\rho} | \Psi \rangle = N \int |\Psi(\mathbf{r}, \mathbf{r}_1, \ldots, \mathbf{r}_{N-1}, \sigma)|^2 d\sigma \, d\mathbf{r}_1 \ldots d\mathbf{r}_{N-1} \tag{3.5}
$$

In Eq. (3.4), the total energy is decomposed into two factors $F[\rho]$ and $V[\rho]$, where the former is a universal, system-independent functional and the latter external potential term contains all system-dependent contributions. The external potential is assumed to be a local multiplicative function, i.e., its value at any point in space depends only on where the function is evaluated and not, e.g., its rate of change. This is not an overly restrictive assumption and it could be relaxed by considering reduced density matrices. The variational principle for wavefunctions (3.2) additionally guarantees that there exists a unique minimum energy density for any external potential. Strictly speaking, the Hohenberg-Kohn theorems hold only for nondegenerate ground state wavefunctions and electron densities that arise from some external potential. These restrictions were subsequently lifted by Levy and Lieb but a detailed treatise is beyond the scope of the present work.

The Hohenberg-Kohn theorems do not provide a concrete tool for solving the ground state electron density that minimizes the total energy because the explicit equation for $F[\rho]$ is unknown. The approximation introduced by Kohn and Sham forms the key step toward an actual computational method. In this framework, the core premise is the introduction of an auxiliary fictitious system composed of noninteracting electrons, $\langle \hat{\mathbf{W}} \rangle = 0$, which is able to reproduce the same density as any given system of interacting electrons. The wavefunction, $|\Psi_{KS}\rangle$, of a noninteracting system of $N$ electrons is antisymmetrically separable and can be expressed as a single Slater determinant built from the $N/2$ lowest energy single-particle states $\{ |\psi_i\rangle \}_{i=1}^{N/2}$, the so-called Kohn-Sham (KS) orbitals. These orbitals are assumed to be orthonormal $\langle \psi_i | \psi_j \rangle = \delta_{ij}$, spin-independent, and doubly occupied without loss of generality. Due to orthonormality, the Slater-Condon rules imply that the electron density from Eq. (3.5) can be expressed in a much simpler form in terms of the Kohn-Sham orbitals

$$
\rho(\mathbf{r}) = 2 \sum_{i}^{N/2} |\psi_i(\mathbf{r})|^2 \tag{3.6}
$$

By comparing the energies of the interacting and noninteracting systems, the total energy of the interacting system with the same electron density as the noninteracting system can be identified as

$$
E[\rho] = T_s[\rho] + E_H[\rho] + V[\rho] + E_{xc}[\rho] \tag{3.7}
$$

where $E_{xc}[\rho]$ is the so-called exchange-correlation functional, $T_s[\rho]$ is the kinetic energy of the noninteracting electrons

$$
T_s[\rho] = \langle \Psi_{KS} | \hat{T} | \Psi_{KS} \rangle = -\frac{1}{2} \sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle \tag{3.8}
$$

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and $E_H[\rho]$ is the classical Coulombic electron-electron interaction energy, or the Hartree energy

$$E_H[\rho] = \frac{1}{2} \int \frac{\rho(r) \rho(r')}{|r-r'|} drdr'$$  \hspace{1cm} (3.9)

The exchange-correlation functional absorbs all many-body contributions to the energy that are not included in the $T_s[\rho]$ and $E_H[\rho]$ terms.\textsuperscript{133} Taking the difference of Eqs. (3.4) and (3.7) indicates that the functional can be rigorously defined as $E_{xc}[\rho] = (W[\rho] - E_H[\rho]) + (T[\rho] - T_s[\rho])$. The Kohn-Sham method would be an exact ground state theory if the exact exchange-correlation functional could be determined. However, this task is unfeasible and the functional must be approximated somehow, a discussion relegated to Sec. 3.3.

The variational principle (3.2) can be leveraged to derive an algorithm for finding the ground state electron density that minimizes the total energy. To that end, Eq. (3.7) is variationally differentiated with respect to $\rho(r)$ subject to the orbital orthonormality constraint $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ and the resulting expression is set to zero. This leads to the Kohn-Sham eigenvalue equations, which are reminiscent of the Schrödinger equation (3.1)\textsuperscript{133}

$$\left( -\frac{1}{2} \nabla^2 + v(r) + v_H(r) + v_{xc}(r) \right) \psi_i(r) = \epsilon_i \psi_i(r)$$  \hspace{1cm} (3.10)

where

$$v_H(r) = \int \frac{\rho(r')}{|r-r'|} dr' \quad \text{and} \quad v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$  \hspace{1cm} (3.11)

The mathematical validity of the Kohn-Sham equations (3.10) is an intricate problem that amounts to proving the existence of the necessary variational derivatives and the coincidence of the sets of interacting and noninteracting electron densities. The exact details have been worked out elsewhere,\textsuperscript{136,140} but suffice to say, the Kohn-Sham method can be applied to virtually any system under rather mild assumptions. It is also interesting to remark that single-particle orbitals $|\psi\rangle$ and an effective wavefunction $|\Psi_{KS}\rangle$ appear in the Kohn-Sham approach despite the original premise of DFT, which was to avoid treating an actual wavefunction through the introduction of the electron density. However, the Kohn-Sham orbitals nor their energies have no real physical meaning, except the highest occupied level,\textsuperscript{133} since they represent fictitious states of a noninteracting system. The Slater determinant constructed from these orbitals is not identical with the interacting ground state $|\Psi\rangle$ for exactly the same reason. A more prudent interpretation of the Kohn-Sham states is that they are a convenient tool to generate the exact ground state electron density, which is fully consistent with the seminal revelation of Hohenberg and Kohn.\textsuperscript{132} As a matter of fact, the use of orbitals is, by no means, mandatory and various orbital-free formulations of DFT have been proposed.\textsuperscript{141}

The Kohn-Sham eigenvalue problem must be solved iteratively because the equations are nonlinear: the potential terms in the parenthesis of Eq. (3.10)
Density Functional Theory
depend on the density, which in turn is a function of the Kohn-Sham orbitals according to Eq. (3.6). In practice, this process involves starting from an initial trial density, computing the total effective potential \( v_{KS}(r) \), and solving the Kohn-Sham equations to generate a new refined density estimate. This density is subsequently used as the trial density of the next iteration. The iteration process is continued until the variation in input and output densities as well as the system energy fall below some predetermined accuracy threshold, an approach that is dubbed the self-consistent field (SCF) method.

One final ingredient is, however, still required to enable Kohn-Sham DFT as a practical computational tool, namely, the introduction of a suitable finite basis to represent the single-particle states. Planewaves, Gaussian-type orbitals (GTOs) or numerical basis sets have traditionally been employed for this task. The simulations in this thesis were performed in the framework of the hybrid Gaussian and planewaves (GPW) method\(^\text{142}\) as implemented in the CP2K\(^\text{143,144}\) software. The GPW method and the main steps of a DFT simulation in CP2K are briefly outlined in the following Sec. 3.2 as it pertains to the current work.

### 3.2 The Gaussian and Planewaves Method

The introduction of a Gaussian basis to express the Kohn-Sham orbitals amounts to expanding the orbitals as a linear combination of \( M \) atomic orbitals (AOs)\(^\text{131}\)

\[
\psi_i(r) = \sum_a c_{ia} \chi_a(r) \tag{3.12}
\]

where \( \chi_a \) are the atomic orbitals and \( c_{ia} \) the molecular orbital (MO) coefficients. The MO coefficients of \( N \) Kohn-Sham states are conveniently arranged into a matrix \( C \in \mathbb{R}^{M \times N} \) in order of increasing orbital energy. With this notation, the variational optimization of the Kohn-Sham functional (3.7) can be reformulated as an energy minimization problem over the molecular orbital coefficients\(^\text{145}\)

\[
C^* = \arg\min_C \{ E[C] \mid C^T S^{AO} C = I \} \tag{3.13}
\]

where \( C^* \) is the optimal choice of \( C \) which minimizes the total energy \( E[C] \) and satisfies the nonlinear orbital orthonormality constraint \( C^T S^{AO} C = I \), \( I \) is the identity matrix, and \( S^{AO} \) is the overlap matrix of the atomic orbitals, composed of elements \( S^{AO}_{a,\beta} = \langle \chi_a \mid \chi_\beta \rangle \). The Kohn-Sham energy functional (3.7) is given in terms of the MO coefficients as

\[
E[C] = \text{tr}(PK) \tag{3.14}
\]

where \( \text{tr} \) denotes the trace of a matrix, \( P = CC^T \) is the density matrix, and \( K \) is the Kohn-Sham matrix defined in terms of AO pairs as

\[
K_{\alpha,\beta} = \langle \chi_\alpha \mid -\frac{1}{2} \nabla^2 + v_{KS} \mid \chi_\beta \rangle \tag{3.15}
\]
On the basis of Eqs. (3.13)-(3.15), the efficient solution of the Kohn-Sham optimization problem requires well-scaling algorithms to build the Kohn-Sham matrix $K$ and to self-consistently minimize the energy under the MO orthonormality condition. The latter task is obviously rather insensitive to the choice of AO basis while the former is entirely governed by it.

The traditional algorithm to optimize the MO coefficients $C$ involves diagonalizing the Kohn-Sham matrix and iteratively improving the MO coefficients by expressing them as a linear combination of previous iterates according to Pulay's\textsuperscript{146} direct inversion in the iterative subspace (DIIS) mixing scheme.\textsuperscript{131} The orthonormality condition is automatically satisfied with this algorithm; however, the method is not guaranteed to converge and it suffers from cubic scaling in the number of Kohn-Sham states owing to the cost of matrix diagonalization. The computational performance can be improved by using more efficient numerical diagonalization libraries with a smaller scaling prefactor,\textsuperscript{147} or by switching to iterative diagonalization algorithms, such as the residual minimization method (RMM-DIIS),\textsuperscript{148} where the diagonalization is performed in a smaller subspace.

Another route to a more efficient solution of Eq. (3.13) is to avoid diagonalization altogether by attempting to minimize the energy directly, which is a task complicated by the need to satisfy the nonlinear orthonormality constraint. In case of nonmetallic systems with a finite band gap, VandeVondele and Hutter\textsuperscript{149} rewrote the optimization problem as a linearly constrained equation

$$
X^* = \arg\min_X \{ E[C(X)] \mid X^T S^{AO} C_0 = 0 \} \quad (3.16)
$$

where $C^* = C(X^*)$, $C_0$ is a set of initial (constant) orbitals which satisfy the orthonormality condition, and the MO coefficients are exponentially transformed according to

$$
C(X) = C_0 \cos U + XU^{-1} \sin U \quad (3.17)
$$

where $U := (X^T S^{AO} X)^{1/2}$. This reparametrization of the MO coefficients is known as the orbital transformation (OT) method and it ensures that the orthonormality of the MO coefficients is satisfied by all $X$ which fulfill the linear constraint $X^T S^{AO} C_0 = 0$. The matrix functions of $U$ can be computed with diagonalization or with a truncated Taylor expansion. The computational efficiency of this algorithm stems from the reformulation of the nonlinear MO orthonormality condition as a linear constraint, which enables the use of standard minimization algorithms to optimize $X$ along a linear gradient, instead of having to perform the optimization along a geodesic as was the case with the original constraint.\textsuperscript{149} The OT method is guaranteed to converge if it is combined with a globally convergent minimizer, such as conjugate gradients, although for well-behaved systems indirect DIIS minimization often results in faster convergence. To further accelerate this algorithm, it is possible to adopt an alternative orbital transformation scheme based on the iterative refinement (IR) expansion, which recasts Eq. (3.16) into an unconstrained minimization
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The Kohn-Sham energy functional minimization must be suitably preconditioned with any OT method to achieve good convergence.\textsuperscript{145,149,150} Having defined how to solve Eq. (3.13) without resorting to expensive diagonalization, the attention is now turned to the efficient construction of the Kohn-Sham matrix $\mathbf{K}$. The hybrid Gaussian and planewaves scheme\textsuperscript{142} implemented in CP2K\textsuperscript{143,144} exploits the unique advantages of both basis set representations to achieve linear scaling computation of $\mathbf{K}$, refer to Fig. 3.1 for a simplified flowchart. Gaussian-type orbitals are used as the primary basis set in the GPW method by expanding the atomic orbitals $\chi(\mathbf{r})$ in terms of primitive Gaussians $g(\mathbf{r})$

$$\chi_a(\mathbf{r}) = \sum_k d_{ka} g_k(\mathbf{r})$$ \hspace{1cm} (3.18)

where $d_{ka}$ are so-called contraction coefficients. Electronic interaction terms involving Kohn-Sham single-particle states, e.g., the kinetic energy expression $T_{\rho}[\rho]$, can be evaluated analytically in terms of the Gaussian primitives with Obara-Saika\textsuperscript{151} recursion rules. In order to evaluate (semi)local real space potential terms, the electron density must first be mapped onto a numerical grid via an operation named collocation

$$\rho(\mathbf{r}) = \sum_{a,\beta} P_{a,\beta} \chi^*_a(\mathbf{r}) \chi_\beta(\mathbf{r})$$ \hspace{1cm} (3.19)

The efficiency of the collocation step is improved by adopting a multigrid approach, i.e., multiple grids with different grid spacings, where more diffuse, slowly varying Gaussian functions are mapped onto coarser grids than compact Gaussians.\textsuperscript{143} The electrostatic terms (electron-electron repulsion, electron-nucleus attraction) are computed with Ewald summation by separating the term into short- and long-range parts. The long-range part of a periodic system is readily computed in reciprocal space by first Fourier transforming the density

$$\rho(\mathbf{G}) = \mathcal{F}(\rho(\mathbf{r}))$$ \hspace{1cm} (3.20)

and subsequently solving the Poisson equation $\nabla^2 v_\text{H}(\mathbf{r}) = 4\pi \rho(\mathbf{r})$ as

$$v_\text{H}(\mathbf{G}) = 4\pi \frac{\rho(\mathbf{G})}{|\mathbf{G}|^2}, \quad \mathbf{G} \neq \mathbf{0}$$ \hspace{1cm} (3.21)

where $\mathbf{G}$ are the reciprocal space lattice vectors.\textsuperscript{85} More elaborate Poisson solvers are required in nonperiodic systems, see e.g. Ref. 152 and references therein. Note that the potential in Eq. (3.21) is defined only for $\mathbf{G} \neq \mathbf{0}$. For $\mathbf{G} = \mathbf{0}$, both the average electrostatic field and the net charge must be equal to zero. The electrostatic potential $v_\text{H}(\mathbf{G} = \mathbf{0})$, by contrast, has no natural zero point, which causes the potential alignment issues discussed in Sec. 2.2.3. A standard convention to normalize $v_\text{H}$ is to set its average in the $\mathbf{G} = \mathbf{0}$ cell to zero.\textsuperscript{85}

When solving the Poisson equation, the reciprocal space electron density $\rho(\mathbf{G})$ is computed subject to the condition that the planewave (PW) expanded density
in real space \( \rho_{\text{PW}}(r) \) must coincide with the Gaussian expanded density \( \rho(r) \), where the former term is

\[
\rho_{\text{PW}}(r) = \sum_G \rho(G) \exp(iG \cdot r) \quad (3.22)
\]

and the number of reciprocal space basis functions is controlled by the PW cut-off threshold.\(^{143}\) Representing core electrons with planewaves is computationally inefficient because a large cutoff is required to capture the rapid fluctuations of density in core regions. This issue can be avoided by treating the core electrons with pseudopotentials\(^ {153-155}\) or, alternatively, by switching to the Gaussian and augmented planewaves framework,\(^ {156}\) which however will not be covered herein.

In a typical pseudopotential calculation, only the first or second valence electron shells of an atom are explicitly considered, while the remaining electrons are combined with the nucleus into an effective ionic core. The contribution of ionic cores to the electrostatic potential must also be included, although this term has not been explicitly indicated above in the Poisson equation.\(^ {143}\)

After the Poisson equation is solved in reciprocal space, the electrostatic Hartree potential must be backtransformed into real space with an inverse Fourier transform \( v_H(r) = \hat{\mathcal{F}}^{-1}(v_H(G)) \). The remaining local real space potential terms, such as the exchange-correlation term (see Sec. 3.3) or the short-range part of the pseudopotential term, are then constructed on the real space grid and combined with the Hartree potential, yielding a total potential \( v_{\text{KS}}(r) \).

The final step of computing the Kohn-Sham matrix \( K \) in the GPW approach involves summing the terms that were analytical in the GTO basis with \( v_{\text{KS}}(r) \) by integrating the latter over the Gaussian functions, \( \langle \chi_\alpha | v_{\text{KS}}(r) | \chi_\beta \rangle \).\(^ {143}\)

![Figure 3.1. Simplified flowchart illustrating how the Kohn-Sham matrix \( K \) is built in the GPW method, which combines multigrid techniques with a primary GTO basis and an auxiliary planewave basis to efficiently compute different interaction terms by switching between data representations. The various steps have been explained in the main text. The notation \( a + b = c \) is shorthand for \( a = a + b \). Adapted from Ref. 143.](image)

### 3.3 The Exchange-Correlation Functional

As defined in Sec. 3.1, the exchange-correlation functional \( E_{\text{xc}}[\rho] \) accounts for the missing contributions of residual kinetic energy and nonclassical electron-
electron interactions in the Kohn-Sham framework, stemming from the introduction of the noninteracting auxiliary system. The exact form of this functional is unknown, necessitating the introduction of a suitable approximative exchange-correlation functional in order to perform numerical simulations with Kohn-Sham DFT. Unfortunately, there is no straightforward prescription to systematically improve the quality of the functional approximation, although the exact functional should obey various theoretical conditions and highly accurate reference data is available for parametrizing the functional in certain systems.\(^{133}\) This has led to the proposal of a great number of functionals that are not universally transferable, i.e., they typically perform better for certain physical or chemical properties, or for specific types of materials, depending on which attributes or systems were considered in developing the functional.

Proposed exchange-correlation functionals can be arranged into a hierarchical structure—a “Jacob’s ladder” toward the heaven of chemical accuracy as popularized by Perdew\(^ {157}\)—based on the locality of the functional and which aspects of the electron density or the Kohn-Sham orbitals are incorporated into the functional. The range of functionals available to electrochemical catalysis applications are primarily limited by the large system sizes required to describe the electrochemical interface. Consequently, generalized gradient approximations (GGA) of the exchange-correlation functional, such as PBE\(^ {158}\) or its revised variants,\(^ {159}\) are commonly employed in such systems. These functionals can be expressed in the following general form\(^ {133}\)

\[
E_{\text{xc}}^{\text{GGA}}[\rho] = \int e_{\text{xc}}(\rho, \nabla \rho) \rho(r) dr
\]  

(3.23)

GGA functionals are semilocal functionals of the electron density \(\rho(r)\), that is, their spatial dependence is restricted to an infinitesimal region around \(r\), making the computational evaluation of GGA functionals relatively inexpensive.

Becke\(^ {160}\) identified the lack of permutation symmetry of the single-particle Kohn-Sham states as one of the primary missing contributions in the exchange term of GGA functionals. In order to solve this issue, he proposed a new class of exchange-correlation functionals, colloquially known as hybrid functionals, which include an admixture of exact exchange from Hartree-Fock theory, expressed in terms of Kohn-Sham orbitals belonging to the same spin channel as

\[
E_x^{\text{HF}} = -\frac{1}{2} \sum_{i,j} \int \psi_i^*(r_1) \psi_j(r_1) \frac{1}{|r_1 - r_2|} \psi_j^*(r_2) \psi_i(r_2) dr_1 dr_2
\]  

(3.24)

Evaluating the integrals in the above equation imposes an order of magnitude increase in computational effort in contrast to standard GGA-level DFT simulations, although truncation and other schemes have been suggested to mitigate the cost, see e.g. Ref. 161 and references therein. This prohibits the routine use of hybrid functionals in kinetic simulations of periodic electrocatalysis systems.

Another detrimental limitation of both GGA and hybrid functionals is the
omission of correlation interactions that arise from electron density fluctuations, the so-called van der Waals interactions, which encompass interactions between induced dipoles (London dispersion force), permanent dipoles (Keesom force), and permanent and induced dipoles (Debye force). The proper inclusion of dispersive interactions is crucial to constructing a realistic description of hydrophobic interfaces, e.g., the carbon nanotube-water interface considered herein. Addressing this issue has prompted the development of a number of different approaches, ranging from nonlocal correlation functionals to semiempirical pairwise models. The most prominent pairwise scheme is the DFT-D3 method proposed by Grimme et al., which was adopted in the present work due to its computational efficiency.

The approximative nature of the exchange-correlation functional is the main source of errors in DFT simulations. In addition to the issues highlighted above, the accuracy of electrocatalytic DFT models is also adversely affected by the aptly named overdelocalization error, which manifests itself as an electron density that is spatially too dispersed in comparison to more accurate methods. The spurious delocalization of electron density artificially stabilizes the transition state configuration, where chemical bonds are elongated from their equilibrium values, leading to an underestimation of the activation energy barrier with DFT. The roots of this problem can be traced to the more fundamental self-interaction error (SIE) which, as the name suggests, implies that electrons interact with themselves, even in single electron systems. This error can readily be identified from the Kohn-Sham expression for the Coulomb energy when the density is expanded in terms of the Kohn-Sham orbitals since the summations over single-particle states do not explicitly preclude interactions between the same pairs of orbitals at different positions, unlike in Hartree-Fock theory. A pathological example of SIE is the dissociation reaction \( \text{H}_2^+ \rightarrow \text{H}^+ + \text{H} \), where the positive charge remains delocalized over both atoms with standard functionals even as the hydrogen separation tends to infinity, see Fig. 3.2.

Another SIE related issue in electrochemical systems is the band alignment problem, which is composed of two contributions. First, DFT predicted band gaps are usually inaccurate when compared to experimental values. Second, the relative positioning of frontier orbitals in isolated systems is often incorrect. In the case of a water-electrode interface, this error can lead to spurious charge transfer between the electrode and water when the components are brought into contact during the construction of a model interfacial system.

Various methods have been proposed to alleviate self-interaction error. One such method is constrained density functional theory (CDFT) which was employed in the current work (Publication IV) to reevaluate the predictions of activation and reaction energies from Publication II. This method is described in detail in the next Section 3.4. Unrelated to reducing SIE, CDFT is also suitable for modeling different electron transfer processes, e.g., within the framework of Marcus theory. This prospect was considered in Publication III and it is another subject that will be discussed in the following section.
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Figure 3.2. Illustration of DFT self-interaction error for the reaction $\ce{H_2^+} \rightarrow \ce{H^+} + \ce{H}$. PBE notably deviates from the exact Hartree-Fock dissociation profile because the positive charge remains delocalized over both atoms regardless of the atomic separation. The correct profile can be recovered with constrained DFT configuration interaction (CDFT-CI) using fragment constraint states $\ket{\ce{H^+H}}$ and $\ket{\ce{HH^+}}$ as the basis, see Sec. 3.4.

3.4 Constrained Density Functional Theory

Constrained DFT is a tool to create density-localized electronic states. The method is an extension of Kohn-Sham DFT as will be rigorously defined in Sec. 3.4.1. The importance of density-localized electronic states in modeling electron transfer and proton-coupled electron transfer reactions will be explored in Sec. 3.4.2. Section 3.4.3 contains a brief description of the algorithms that were implemented in this work to perform CDFT simulations in CP2K.

3.4.1 Theoretical Foundations

The use of approximate exchange-correlation functionals can lead to a spurious overdelocalization of the electron density, as was discussed in Sec. 3.3. In constrained DFT, this issue is explicitly prevented by supplementing the standard Kohn-Sham energy functional with suitable external potentials within an extended Lagrangian scheme. Concretely, the CDFT energy functional with $M$ arbitrary density constraints can be defined as the dual optimization problem

$$ E_{CDFT}[\rho(r), \xi] = \max_{\xi} \min_{\rho(r)} \left( E[\rho(r)] + \sum_{c} \xi_c \left[ \sum_{\sigma=\uparrow,\downarrow} \int w_\sigma^c(r) \rho_\sigma(r) dr - N_c \right] \right) $$

$$ =: \max_{\xi} \min_{\rho(r)} \left( E[\rho(r)] + V_{CDFT}[\rho(r), \xi] \right) \quad (3.25) $$

where the shorthand $\rho_\sigma^c(r) := \rho(r, \sigma)$ has been introduced for the spin density $\rho(r, \sigma)$, which is computed analogous to Eq. (3.6) but over singly occupied spin-dependent orbitals $\psi_i(r, \sigma)$, $\xi$ are the Lagrange multipliers associated with the constraints, and $N_c$ is the constraint target value. The term $w_\sigma^c(r)$ is an atom-centered real space weight function that enforces the desired density localization.
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by operating on the density. The conventions \( w^\uparrow_c = w^\downarrow_c = w_c \) and \( w^\uparrow_c = -w^\downarrow_c = w_c \) are adopted to treat total \((\rho^\uparrow + \rho^\downarrow)\) and magnetization \((\rho^\uparrow - \rho^\downarrow)\) density constraints, respectively. Inspection of Eq. (3.25) reveals that the constraint potentials can be interpreted as an additional penalty term: the more the unconstrained Kohn-Sham DFT ground state density deviates from the wanted localized solution, the larger values \( \xi \) will attain since these measure the strength of the constraint potentials. Any population analysis scheme can be used to define the weight function \( w^\sigma_c(r) \), although the accuracy of real-space-based methods is generally reported to be superior to orbital-dependent methods.\(^{15}\) The Becke real space density partitioning method has been used throughout this thesis, see Sec. 3.4.3 for a detailed overview.

The constraint target value, \( N_c \), is a measure of the desired number of valence electrons that should be localized on a particular set of atoms. As an alternative to using the formal number of electrons per atom or molecule in \( N_c \), which can be an ill-behaved approach when attempting to constrain the densities of strongly interacting molecules, e.g., during a chemical reaction, it is also possible to employ so-called fragment-based constraints.\(^{169,171}\) In this scheme, the system is first split into two isolated fragments, \( I = \{A, B\} \), depending on the modeled phenomenon, see Fig. 3.3 for a practical example. The spin densities, \( \tilde{\rho}^\sigma_I(r) \), of these fragments are then separately optimized. Finally, a CDFT simulation for the actual interacting system is commenced where the constraint target values are computed from the superimposed isolated densities according to

\[
\tilde{N}_c = \sum_{\sigma = \uparrow, \downarrow} \int w^\sigma_c(r)(\tilde{\rho}^\sigma_A(r) + \tilde{\rho}^\sigma_B(r))dr
\]  

(3.26)

Observe that the number of electrons localized onto any atomic group is no longer an integer value when using fragment constraints. Furthermore, the constraint target values are now also dependent on atomic positions, which is beneficial when modeling (electro)chemical reactions along a reaction coordinate.

The addition of the CDFT constraint potential functional, \( V_{\text{CDFT}}(\rho, \xi) \), to

**Figure 3.3.** Using fragment densities, \( \tilde{\rho}^\sigma_I(r) \), to define CDFT constraints with Eq. (3.26). In this example, charge transfer between the water molecules is prevented by the constraint.
the Kohn-Sham energy functional in Eq. (3.25) implies that the Kohn-Sham eigenequations (3.10) must be modified accordingly. For a given spin \( \sigma \), differentiation of \( V_{\text{CDFT}}[\rho, \xi] \) yields a new potential term \( v_{\text{CDFT}}[\rho^\sigma(r)] = \sum_c \xi_c w^\sigma_c(r) \). The solution of the CDFT Kohn-Sham equations is more complicated than the standard KS problem because an extra optimization step is needed to fix the values of the constraint Lagrange multipliers \( \xi \), in addition to the normal SCF loop where total energy is minimized by varying the electron density. In practice, the stationary point of \( E_{\text{CDFT}}[\rho, \xi] \) can be solved by alternating between energy minimizations along \( \rho(r) \) and maximizations along \( \xi \) until self-consistency is reached; the secondary optimization is a maximization problem because the Hessian—the matrix of second partial derivatives—of \( E_{\text{CDFT}}[\rho, \xi] \) is negative semidefinite with respect to differentiation in \( \xi \).\(^{166,167,172}\) An algorithm to solve (3.25) will be introduced later in Sec. 3.4.3. Finally, it is worth noting that atomic forces needed, e.g., to perform CDFT-based molecular dynamics simulations must also be supplemented by a term arising from the density constraints

\[
F_i^{\text{CDFT}} = -\nabla_i V_{\text{CDFT}}[\rho(r), \xi] = -\sum_c \xi_c \sum_{\sigma = \uparrow, \downarrow} \int \frac{\partial w^\sigma_c(r)}{\partial R_i} \rho^\sigma(r) dr \tag{3.27}
\]

### 3.4.2 Diabatic States in (Proton-Coupled) Electron Transfer

The electronic states produced by a CDFT simulation are density-localized diabatic states, as opposed to the adiabatic states from standard DFT computations.\(^{173,174}\) By definition, a diabatic electronic state retains its physical character during a reaction as the system traverses the reaction coordinate. Diabatic states are a central concept in various electron transfer theories. For instance, in Marcus theory of homogeneous electron transfer, the reaction is described as a transition between diabatic states corresponding to the reactant and product configurations, e.g., as \( |A^- + B\rangle \rightarrow |A + B^-\rangle \).\(^{14}\) The relationship between diabatic and adiabatic electronic states in Marcus theory has been visualized in Fig. 3.4. Within this framework, the rate constant of an electron transfer reaction that spans both the adiabatic and diabatic regimes can be derived by combining harmonic transition state theory with Landau-Zener (LZ) theory, yielding the following general expression\(^{14,44,175}\)

\[
k_{\text{ET}} = \kappa \zeta_n \exp \left[ -\frac{(\lambda + \Delta G)^2}{4k_B T \lambda} + \frac{\Delta}{k_B T} \right] \tag{3.28}
\]

where \( \kappa \in [0,1] \) is the electronic transmission coefficient, \( \zeta_n \) is an effective nuclear frequency along the ET reaction coordinate, \( \lambda \) is the (effective) solvent reorganization free energy, \( \Delta G \) is the reaction free energy and \( \Delta \) is an adiabacity correction,\(^{176}\) which tends to zero in the limit of vanishing electronic coupling between diabatic states (see below). The first term in the exponential can be identified as the activation free energy \( G^\Delta := (\lambda + \Delta G)^2/(4\lambda) \) for diabatic electron transfer, refer to Fig. 3.4 for a visual interpretation. The free energy quantities
Figure 3.4. Free energy curves for outer sphere ET within the Marcus formalism. The ground and first excited adiabatic electronic states are shown by solid lines, whereas dashed lines depict the reactant and product diabatic states. The adiabatic states were obtained from the diabatic states with CDFT-CI, see Eq. (3.32). The energy quantities involved in the rate constant expression (3.28) are indicated. Here, $\lambda_a$ denotes the free energy required to change the equilibrium configuration of diabatic state $a$ to the equilibrium configuration of state $b$ while remaining on the free energy curve of state $a$. The analogously defined quantity $\lambda_b$ is not shown for clarity. Adapted from Ref. 14.

$\lambda$ and $\Delta G$ can be evaluated by sampling the vertical energy gap between the two diabatic states, which can readily be computed with CDFT, see Sec. 4.2.

The magnitude of $\kappa$ is determined by the probability $P_{\text{LZ}}$ the system transitions from the reactant (a) diabatic state to the product (b) state according to

$$
\kappa = \begin{cases} 
2P_{\text{LZ}}, & \text{if } \Delta G \geq -\lambda \\
1 + P_{\text{LZ}}, & \text{if } \Delta G < -\lambda 
\end{cases}
$$

(3.29)

$$
P_{\text{LZ}} = 1 - \exp\left(-2\pi\gamma\right) = 1 - \exp\left(\frac{\pi^{3/2} \langle |H_{ab}|^2 \rangle_{T}}{\hbar \xi_n \sqrt{\lambda g B T}}\right)
$$

(3.30)

Above, $|H_{ab}|$ denotes the electronic coupling between ET states, defined rigorously in terms of the diabatic $N$-electron wavefunctions $|\Psi_i\rangle$ and the electronic Hamiltonian $\hat{H}$ as $H_{ab} = \langle \Psi_a | \hat{H} | \Psi_b \rangle$, $\hbar$ is Planck’s constant, while $\langle \cdot \rangle_{T}$ denotes thermal averaging over nuclear configurations sampled from the canonical ensemble. The value of the electronic coupling can be estimated from CDFT, as will be shown below. The term $2\pi\gamma$ gauges the electron transfer reaction’s degree of electronic adiabacity. When $2\pi\gamma \gg 1$, the reaction is adiabatic and the system remains on the ground adiabatic electronic state as it traverses the reaction coordinate; whereas at the opposite limit, $2\pi\gamma \ll 1$, an abrupt transition from the reactant diabatic state to the product state occurs with probability $P_{\text{LZ}}$ at the crossing region where the states become degenerate.

The preceding theory holds for homogeneous outer sphere electron transfer reactions in a dielectric medium, e.g., for intramolecular ET within a mixed-
valence compound as considered in Publication III. However, this rate expression is no longer valid in the case of heterogeneous ET where a solid electrode acts as the electron donor or acceptor. The primary difference between homogeneous and heterogeneous ET is the active involvement of multiple electronic states of the electrode in heterogeneous ET, which can have a profound impact on the rate of electron transfer, especially on metallic electrodes with a dense electronic density of states. Although heterogeneous ET reactions are not explicitly considered herein, a brief digression is warranted to establish a connection between heterogeneous ET and the HER catalysis model proposed by Schmickler et al.,⁴³ which was discussed back in Secs. 2.1 and 2.2.2. On a qualitative level, the participation of multiple electrode states suggests that in order to derive a proper rate expression for heterogeneous ET, the rate expression should be integrated over the electrode's DOS and suitably weighted by the Fermi-Dirac distributed orbital occupations, see for example Refs. 26,44,45 for a more quantitative analysis. The electronic coupling will again measure the strength of the interactions between the electrode states and the frontier orbital of the reacting species, but this quantity will now also exhibit an explicit dependence on the electrode’s electronic states, and its magnitude will in general not be constant for all orbital pairs. The occupations of the electrode states, and hence the rate of electron transfer, can be altered by applying an overpotential $\eta$, as was described in Sec. 2.2.2. Based on the preceding discussion, it is readily apparent that a theory of heterogeneous ET is, in many respects, fully analogous to an electronic theory of HER, even though the latter is further complicated by the necessity to treat inner sphere effects, i.e., the formation of a covalent bond between the proton and the electrode. Another complementary perspective will be offered below.

It is possible to recover adiabatic electronic states and their energies from a set of diabatic states through configuration interaction (CI). Performing CI calculations within the framework of CDFT (CDFT-CI), therefore, provides a tool to estimate the severity of charge overdelocalization effects in DFT simulations, assuming a suitable basis of diabatic states can be constructed for the modeled system, see also Fig. 3.2.¹⁶⁸,¹⁶⁹ A minimal basis for any electrochemical reaction includes just the reactant and product diabatic states, which are generated by enforcing different density localization criteria in Eq. (3.25). Naturally, CDFT is incapable of producing actual $N$-electron diabatic wavefunctions that are eigenvectors of the exact electronic Hamiltonian because the method is based on Kohn-Sham DFT. The diabatic Slater determinants from CDFT can nevertheless be used as approximations of the interacting wavefunctions, as long as the accuracy of this approach is carefully validated, see Sec. 4.2 and Publication III.

In practice, a CDFT-CI calculation involves expanding the system’s adiabatic electronic state as a linear combination of the CDFT determinants $|\Psi_{i}^{\text{CDFT}}\rangle$

$$|\Psi\rangle = \sum_{i} c_{i} |\Psi_{i}^{\text{CDFT}}\rangle, \quad \sum_{i} c_{i}^{2} = 1 \quad (3.31)$$

where the squares of the expansion coefficients, $c_{i}^{2}$, describe the weight each
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CDFT state contributes to the adiabatic state \(|\Psi\rangle\). The adiabatic states and their energies are obtained by solving the generalized eigenvalue equation

\[
HC = SCA, \quad H_{i,j} = \langle \Psi_i^{\text{CDFT}} | \hat{H}_{\text{KS}} | \Psi_j^{\text{CDFT}} \rangle
\]

where \(H\) is the effective Hamiltonian matrix, \(\hat{H}_{\text{KS}}\) is the Kohn-Sham Hamiltonian operator, \(C\) is the matrix of expansion coefficients, \(\Lambda\) is a diagonal matrix containing the eigenvalues of \(H\), and \(S\) is the overlap matrix of the diabatic states, comprised of terms \(S_{i,j} = \langle \Psi_i^{\text{CDFT}} | \Psi_j^{\text{CDFT}} \rangle\). The diagonal of \(H\) contains the energies of the diabatic CDFT states, while the off-diagonal elements \(H_{i,j} = H_{j,i}\) are calculated according to the following equation to ensure \(H\) is symmetric\(^1\)

\[
H_{i,j} = \frac{E_i^{\text{CDFT}} + E_j^{\text{CDFT}}}{2} S_{i,j} - \sum_c \left( \langle \Psi_i^{\text{CDFT}} | \xi_c^i w^c(r) + \xi_j^j w^c(r) | \Psi_j^{\text{CDFT}} \rangle \right) \quad (3.33)
\]

The summation above should be understood as an operation over spin-dependent Slater determinants although explicit spin dependence has been omitted on the basis of \(w_c(r)\) spin conventions defined in Sec. 3.4.1. Note that the electronic coupling \(|H_{ab}|\) discussed above in relation to the Marcus rate equation (3.28) does not exactly equal the sole off-diagonal element of \(H\) when a two diabatic state basis is employed. This is due to the fact that the electronic states required in computing \(|H_{ab}|\) should be orthogonal to each other, whereas CDFT Slater determinants usually have a nonvanishing overlap.\(^1\) The CDFT states can, however, be orthogonalized, e.g., by applying symmetric Löwdin orthogonalization to \(H\), which produces a new matrix \(H'\) whose off-diagonal element is now the sought after value of \(|H_{ab}|\). In the more general case that the adiabatic state is expanded in terms of more than two diabats, \(|H_{ab}|\) is given by the vertical energy splitting of the first excited and ground adiabatic electronic states at the transition state, as depicted in Fig. 3.4.\(^1\)

A particularly appealing application of CDFT-CI is to reexamine DFT predicted values of activation and reaction energies for electrocatalytic reactions because, as highlighted in Sec. 3.3, these quantities are prone to spurious density delocalization errors. This methodology was originally suggested by Van Voorhis and coworkers\(^1\) who applied the approach to simple gas phase chemical reactions. The authors were successful in demonstrating that CDFT-CI improved the accuracy of activation energies computed with the BLYP and B3LYP functionals in comparison to high-level reference data, which was attributed to an enhanced density localization. Motivated by their success, the effects of CDFT-CI on the kinetic parameters of CNT-catalyzed HER were explored in Publication IV by reexamining a subset of the reaction energy paths originally characterized in Publication II with standard DFT. The Soudackov–Hammes-Schiffer (SHS) theory of proton-coupled electron transfer\(^1\) was adopted to define the relevant diabatic states for the elementary reaction steps of HER. Two extra diabatic states in addition to the reactant and product diabats were introduced in the CDFT-CI model, as will be subsequently shown in Sec. 4.1.3.
Before concluding this section, a few remarks about the versatility of SHS theory and its direct applicability to surface-catalyzed PCET reactions are in order, although this connection was not extensively explored within the scope of this work. In contrast to Marcus theory where all nuclei are assumed to be classical particles, SHS theory treats the reacting proton on an equal quantum mechanical footing to the electronic subsystem by solving the nuclear Schrödinger equation. Diabatic vibronic wavefunctions, composed of an electronic and a proton nuclear part, assume an analogous role to diabatic electronic states in pure electron transfer theories. Many biological PCET processes have been shown to exhibit vibronic diabacity, underlining the importance of explicitly treating protons as quantum particles. The concept of (varying) electrode potential can be included in SHS theory either through model Hamiltonian approaches or by including the electronic DOS from DFT in the PCET rate equation. In the future, combining grand canonical formulations of DFT, which were discussed in Sec. 2.2.3, with SHS theory could prove to be a formidable method in the investigation electrocatalytic processes in addition to the widely employed kinetic- and descriptor-based approaches. However, within the context of this thesis, I wish to emphasize that SHS theory has been used solely as a tool to define the diabatic states for CDFT-CI simulations of HER, whereas the main focus is placed on refining DFT predicted activation and reaction energies.

### 3.4.3 Implementation in CP2K

Algorithms to perform CDFT simulations in CP2K were implemented Publications III-IV. The main aspects of the implementation will be described in this section with the flowchart of Fig. 3.5 serving as a visual reference.

As stated earlier in Sec. 3.4.1, the CDFT Kohn-Sham optimization problem defined by Eq. (3.25) can be solved iteratively using a two-tiered self-consistent field approach of alternating energy minimizations along $\rho(r)$ and maximizations along $\xi$. The orbital transformation SCF algorithm has been used throughout this work for the inner loop energy minimization with a fixed value of $\xi$, although the implemented CDFT scheme is also compatible with traditional diagonalization-based solvers. An algorithm for the outer energy maximization along $\xi$ can be derived by first noting that the exact solution should satisfy

$$c(\xi) = \left[ \sum_{\sigma=\uparrow,\downarrow} \int w^\sigma_1(r) \rho^\sigma(r) dr - N_1, \cdots \right]^T = 0 \tag{3.34}$$

The introduced function $c$ does not depend on $\xi$ directly but a parametric dependence arises because the inner loop minimization of the energy produces a unique density $\rho(r)$, and thus a new value of $c$, for any fixed value of $\xi$. The task of maximizing the energy with respect to $\xi$ can be viewed as a root finding problem according to Eq. (3.34), which can be terminated when a value of $\xi$ is found that satisfies $\max|c(\xi)| \leq \epsilon$ at some fixed convergence threshold $\epsilon$. The necessary conditions to guarantee the uniqueness of this solution have been
analyzed in the literature. Standard multivariate root finding algorithms may be utilized to iteratively solve $\max|e(\xi)| \leq \varepsilon$. A quadratic convergence to the unique root can be achieved by adopting the Newton-Raphson method, assuming $c$ is regular and differentiable. In this algorithm, a new guess for $\xi_n$ at step $n$ is generated from the previous iteration according to

$$\xi_n = \xi_{n-1} - \beta J^{-1}_n c(\xi_{n-1})$$

(3.35)

where $\beta > 0$ is a step size and $J^{-1}$ is the inverse of the Jacobian matrix, or the matrix of first partial derivatives. The step size is optimized on each iteration with backtracking line search, i.e., by incrementally reducing the step size until it no longer reduces the self-consistently evaluated CDFT convergence criterion $\max|e(\xi)|$, or the maximum number of line search iterations is reached. The Jacobian matrix is approximated with finite differences since analytical
gradients are not available. For robust optimization, a first-order forward difference stencil often suffices and the elements of $J$ can be computed as

$$ J_{ij} = \frac{\partial c_i}{\partial \xi_j} \approx \frac{c_i(\xi + \delta_j) - c_i(\xi)}{\delta_j} $$

where $\delta_j$ is a small perturbation of the $j$th component of $\xi$. Evaluating the Jacobian matrix self-consistently is a rather expensive computational operation when multiple density constraints are imposed on the system. The cost can be mitigated by reusing $J$ for multiple iterations or by updating the matrix iteratively in the spirit of Broyden’s method and other quasi-Newton methods. Gradient bisection is a cheap alternative algorithm for systems with a single constraint, although the method exhibits only linear convergence. Such approaches are, however, rarely necessary when a preexisting CDFT solution is available for restarting the simulation, e.g., from the previous time step in an MD simulation, or from the previous configuration along a discretized reaction coordinate.

The density constraints in Eq. (3.25) were enforced throughout this thesis by assigning each atom a volume according to the real space partitioning method proposed by Becke. This method can be considered as a smoothed analogue of Voronoi partitioning, see illustration in Fig. 3.6. Electrons are localized onto a set of atoms, $W_c$, by constructing the CDFT weight function $w_c(r)$ as a weighted sum of atomic Becke weight functions

$$ w_c(r) = \sum_{i \in W_c} d_i P_i(r) $$

where $N$ is the set of all atoms in the system and $P_i(r)$ are so-called cell functions, constructed from the products of smoothed polynomial step functions,
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\( s(\omega_{ij}) \). The function argument, \( \omega_{ij} \), is the hyperboloidal coordinate function

\[
\omega_{ij}(\mathbf{r}) = \frac{|\mathbf{R}_i - \mathbf{r}| - |\mathbf{R}_j - \mathbf{r}|}{|\mathbf{R}_i - \mathbf{R}_j|}
\]  

(3.38)

Atomic size information can be incorporated into Becke partitioning by introducing an offset term into \( \omega_{ij} \) which depends on the relative sizes of atoms.\(^{170}\) Although atomic radii are not uniquely definable, the results are rather insensitive to the selected definition as long as consistency is maintained. Atomic size adjustments are mandatory to obtain physically reasonable partial charges.

Examination of Eqs. (3.37)-(3.38) suggests that a naive implementation of Becke constraints in CDFT will scale very poorly with system size (number of atoms, system volume, real space grid spacing) because evaluating \( w_c(\mathbf{r}) \) and its atomic gradients requires iterating over all atom pair permutations at every real space point \( \mathbf{r} \). This effectively prohibits the use of such constraints in condensed phase molecular dynamics simulations. Fortunately, the efficiency of the Becke partitioning algorithm can be improved notably. A two order of magnitude improvement was achieved in Publication III by leveraging the properties of the underlying functions. The introduced improvements are summarized below

- \( w_c(\mathbf{r}) \) and its gradients do not depend on \( \rho(\mathbf{r}) \), implying that both can be built and stored in memory before initiating the SCF process.
- For any fixed atom, the atomic Becke weight function will quickly tend to zero as a function of distance, especially in the condensed phase. The weight function can thus be truncated after an element-specific cutoff.
- The weight function \( w_c(\mathbf{r}) \) and its gradients vanish beyond a cutoff radius from all constraint atoms \( W_c \), making it unnecessary to explicitly iterate over the entire domain of the density. Most of the irrelevant grid points can efficiently be discarded by confining the CDFT calculation to a smaller subspace spanned by spherical Gaussians centered on the constraint atoms.
- Iteration over all atom pair permutations can be avoided by exploiting the symmetry properties of the underlying functions.

In order to evaluate properties between different CDFT diabatic states, e.g., to perform CDFT-CI simulations, overlap and interaction integrals between CDFT Slater determinants must be computed, see Eqs. (3.32)-(3.33). Löwdin’s\(^{180}\) rules are adopted to evaluate these integrals as the determinants and the underlying AOs are both nonorthogonal. In practice, the actual Slater determinants are never explicitly constructed since the matrix representation of the weight function, \( \langle \chi_\alpha | w_c(\mathbf{r}) | \chi_\beta \rangle \), and the molecular orbital coefficient \( C \) and atomic orbital overlap \( S_{AO} \) matrices are sufficient to evaluate the integrals, see also Ref. 181.
4. Results and Discussion

This chapter summarizes the main results obtained in this thesis. Sec. 4.1 focuses on simulations of carbon nanotube-catalyzed hydrogen evolution, while the applications of CDFT to homogeneous electron transfer are discussed in Sec. 4.2. More detailed accounts are available in the original peer-reviewed research papers I-IV, which are included as appendices.

4.1 Carbon Nanotube-Catalyzed Hydrogen Evolution

The construction of a realistic kinetic model for simulating HER catalysis on carbon nanotubes was one of the primary objectives of this thesis. Such models should ideally account for electrode potential, hydrogen coverage, and other factors as outlined in Chapters 2-3. A baseline for CNT HER reactivity was established in Publication I (Sec. 4.1.1) by considering the first two factors, where the simplest nitrogen-doped CNT was additionally simulated for comparison. The effects of the carbon ring size on reactivity were subsequently investigated in Publication II using open-ended CNTs (Sec. 4.1.2). Finally, the magnitude of self-interaction error induced uncertainties in predicted HER activation and reaction energies were estimated with CDFT-CI in Publication IV (Sec. 4.1.3).

4.1.1 Electrode Potential and Substitutional Nitrogen Doping Effects

A computational model of the CNT-water system was created by solvating a (14,0) CNT with 331 explicit water molecules, as shown in Fig. 4.1a. The length of the nanotube was confirmed to be sufficient for Γ-point only simulations. The validity of the computational setup, mainly the use of the PBE exchange-correlation functional, was confirmed by estimating the NCNT potential of zero charge (PZC) from a 6.5 ps molecular dynamics simulation. The electrode potential was sampled every 0.25 ps yielding a PZC estimate which agreed with experimental measurements on a mixture of pristine CNTs with different radii after accounting for the effects of nitrogen doping, at least on a semiquantitative level. Moreover, the introduction of solvent was found to alter the NCNT
Figure 4.1. a) Snapshot of the investigated NCNT system. Carbon is gray, nitrogen yellow, oxygen red, hydrogen white, and the periodic boundaries blue. The surrounding vacuum layer has been truncated for clarity. b) Volmer reaction MEPs for different system charges \( q \) on NCNT. c) Fitting of quadratic model to calculated reaction state energies vs. electrode potential to obtain grand canonical energies. d) Grand canonical activation energies for the Volmer step. e-f) Potential-dependent free energy diagrams for the Volmer-Heyrovsky mechanism on NCNT (e) and CNT (f).

work function \( \Phi \) only minimally, 0.1 eV, when averaged over the MD trajectory, which indicates that some charge is transferred from the electrode to water, but that the magnitude is not unphysically large.\(^{13,77}\) A random snapshot from the molecular dynamics simulation was selected for subsequent kinetic calculations after the addition of an extra proton and geometry optimization.

A series of hydrogen adsorption energy, \( \Delta E_{\text{H}}^{\text{ads}} \), calculations were performed in vacuum at the zero hydrogen coverage limit to identify the most prominent site for HER catalysis on NCNT, which is equivalent to a free energy \( \Delta G_{\text{H}}^{\text{ads}} \)-based analysis as the inclusion of entropic and zero-point vibrational effects amounts to an approximately constant shift of \( \Delta E_{\text{H}}^{\text{ads}} \), see note in Sec. 2.1. On the basis of the screening procedure, a carbon site directly adjacent to the nitrogen dopant was predicted to be the most active site owing to a \( \Delta E_{\text{H}}^{\text{ads}} \) closest to thermoneutrality: \(-0.06\) eV vs. 0.85 eV on pristine CNT.\(^{37}\) Direct binding to the nitrogen atom was discovered to be energetically highly unfavorable.

Electrode-potential-dependent activation and reaction energies were derived for the Volmer-Heyrovsky mechanism of HER using the modified double reference method outlined in Sec. 2.2.3. In brief, this process involves computing minimum energy paths for both elementary steps at multiple system charges \( q \) with NEB (Fig. 4.1b), converting the electrode Fermi levels \( \mu \) to absolute potentials \( U_{\text{abs}} \) with Eqs. (2.7) and (2.9), fitting a quadratic capacitance model to the energy vs. potential data to obtain grand canonical energies \( \Omega(U) \) (Fig. 4.1c), and appropriately subtracting the resulting fits (Fig. 4.1d). The scheme presented in Fig. 2.3 was finally leveraged to create (free) energy diagrams for the full reaction mechanism (Figs. 4.1e,f). The Volmer-Tafel mechanism was not modeled in detail since preliminary barrier calculations revealed that the Tafel barrier is at least twice as large as the Heyrovsky barrier on NCNT at similar surface conditions.
Contrary to initial expectations based on $\Delta E_{\text{ads}}^H$ data, the potential-dependent results suggested that the introduction of a single substitutional nitrogen dopant did not in fact improve HER kinetics on CNT as the performance was actually slightly worsened due to a higher ($\approx 0.2$ eV) Heyrovsky barrier and less exothermic reaction energy. These discrepancies were, however, noted to be partly artificial because the initial position of the proton-donating Zundel cation, relative to the nitrogen dopant, was found to influence barriers and reaction energies by $0.1 - 0.2$ eV. Regardless, the results clearly indicated that the Heyrovsky step is the rate-limiting step on both nanotubes owing to a larger barrier than the Volmer step, which agrees with experimental Tafel slope analysis on a variety of functionalized CNTs. Both CNTs are relatively poor HER catalysts as evident from the pristine CNT kinetic barrier at $U = 0$ V vs. SHE that is roughly 0.3 eV larger (1.1 vs. 0.8 eV) than the estimate on Pt(111), evaluated with a different potential correction scheme and a slightly different computational setup. Overall, the calculated Volmer-Heyrovsky barriers are in good agreement with prior studies of pristine and Fe-encapsulated CNTs, though our Volmer values are slightly smaller, perhaps due to differences in the treatment of solvation and other methodological differences. Later simulations by Tuomi et al. are also in accordance with the results of Publication I, see further discussion below.

The modified double reference method produces a reasonable potential dependence for HER, i.e., the kinetics of both reaction steps accelerate as a negative overpotential is applied. Even the unambiguity of selecting where to align the charged and neutral system electrostatic potentials (Eq. (2.9) and Fig. 2.5) vanishes when considering relative energies along a reaction coordinate, see Supporting Information of Publication I. Unfortunately, the scheme does not eliminate the presence of the compensating background charge, which was combated by using a large simulation supercell and a significant number of explicit water molecules. Consequently, the results can be considered semiquantitative at best, as was discussed in more depth in Sec. 2.2.3, enabling the comparison of similarly modeled systems but not a fully rigorous comparison to other systems or other electrode potential controlling schemes. These difficulties do not, however, hinder the evaluation of doping effects studied herein.

The effects of hydrogen coverage are crucial to HER catalysis as discussed in Sec. 2.2.4. Repeating the $\Delta E_{\text{ads}}^H$ calculations by varying the local hydrogen coverage around the active site revealed strong neighbor-neighbor interactions between adjacent sites. Two opposing effects were discovered. Adsorption energies tended to decrease, i.e., become more exothermic, when a site directly adjacent to the active site was already occupied by a hydrogen atom, whereas the opposite was observed when a site two carbon-carbon bonds distant was occupied. A large range of adsorption energies was observed when the local hydrogen coverage was varied. By virtue of the Brønsted-Evans-Polanyi relations, configurations that increase $\Delta E_{\text{ads}}^H$ should be more reactive toward the Heyrovsky step, while the converse should apply to the Volmer reaction. This effect was explored by repeating the kinetic HER simulations for both nanotubes.
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Figure 4.2. a) Hydrogen-coverage-dependent Heyrovsky activation energies. \( \Delta E_{\text{H}}^{\text{ads}} \) is used as the descriptor to distinguish different coverages, resulting in a rather linear dependence between plotted quantities. The range of observed \( \Delta E_{\text{ads}}^{\text{H}} \) for different coverages is indicated by the colored segment on the horizontal axis. b) Coverage-dependent Volmer-Heyrovsky energy diagrams obtained from the fitted linear functions.

at charge neutral conditions by selecting two representative hydrogen coverages with lower and higher values of \( \Delta E_{\text{ads}}^{\text{H}} \) than the bare NCNT surface.

The coverage dependent reaction and activation energies were represented as linear functions of \( \Delta E_{\text{ads}}^{\text{H}} \), as exemplified in Fig. 4.2a, which acts as a relatively good descriptor of the local hydrogen coverage conditions as measured by the goodness of fit. The fitted linear dependencies facilitate the construction of Volmer-Heyrovsky energy diagrams for any fixed static hydrogen coverage solely by computing \( \Delta E_{\text{ads}}^{\text{H}} \) to the active site at that coverage, see examples in Figs. 4.2b,c. This approach is orders of magnitude cheaper than performing actual NEB simulations for each coverage, but it is of course an oversimplification in comparison to a precise microkinetic model since the sites are assumed to be noninteracting.

Nevertheless, this simple model is able to demonstrate that, even in the limit of monolayer hydrogen coverage, the catalytic performance of NCNT is on par with pristine CNT, reinforcing the earlier conclusion that the carbon atom adjacent to a substitutional nitrogen dopant is not activated by doping. This conclusion is in agreement with the results of Deng and coworkers\textsuperscript{10} who showed that despite a similar reduction in \( \Delta E_{\text{ads}}^{\text{H}} \), kinetic HER barriers were not improved by substitutional nitrogen doping of a Fe-encapsulated CNTs. A similar disparity between adsorption energies and reaction kinetics have also been reported on singly- and doubly-doped CNTs in relation to both the hydrogen and oxygen evolution reactions.\textsuperscript{183,185} This work and the other mentioned studies highlight the difficulties related to adopting the descriptor-based model to understand catalytic trends on heterogeneous materials, underlining the importance of accounting for kinetic effects in DFT simulations of such systems.

Seeing as experimental measurements indicate an up to 400 mV decrease in the onset potential of HER due to nitrogen (co)doping, see e.g. Refs. 10,183,184, different doping configurations, i.e., more complex arrangements of substitutional and other nitrogen dopants, or different active sites must be responsible...
for the enhanced activity. From a practical computational perspective, the local hydrogen coverage and the order of filling the surface sites are other variables that warrant more careful attention, which in principle could be addressed by kinetic Monte Carlo modeling—an approach that becomes computationally very demanding in heterogeneous systems.

### 4.1.2 Ring Size Effects

The reactivity of different carbon ring structures toward HER was investigated in Publication II using open-ended CNTs, built by cutting periodic CNTs of chiralities (17,0) and (10,10) perpendicular to the length axis as shown in Fig. 4.3a. The edges of the nanotubes were hydrogen terminated with 1-2 hydrogens depending on site because calculated adsorption energies to these sites were extremely exothermic. Following geometry optimizations, this treatment resulted in the formation of carbon 5-rings and fused 5-rings in addition to the normal 6-rings, see inset in Fig. 4.3a. The Volmer-Heyrovsky activity of the labeled surface sites in these ring structures was investigated using the same methodology employed in Publication I and described previously in, e.g., Sec. 4.1.1. Three representative local hydrogen coverages were selected for NEB-based kinetic barrier calculations. As the main difference to Publication I, the nonperiodic CNTs were not fully solvated and, instead, a simplified droplet model with 15 water molecules was adopted to reduce computational cost. Electrode potential effects were also not considered as an initial approximation, which should not hinder the determination of a relative activity ordering for different surface sites. The Tafel mechanism was again deemed energetically unfavorable.

Equivalent corner sites (3, 7' and 11' in Fig 4.2a) closest to the inert edge of the CNTs were determined to be the most active sites toward HER, at least

![Figure 4.3. a) Structures of investigated open-ended CNTs presenting different ring structure terminations. The sites are labeled according to the inset. b) Computational volcano plots for equivalent corner sites 3, 7' and 11' based on NEB activation energies. c) Representative Volmer-Heyrovsky energy diagrams for the aforementioned sites.](image-url)
on the 5-ring terminated CNT. A computational volcano plot relating the local hydrogen coverage, as described by $\Delta E_{\text{ads}}^H$, and the Volmer-Heyrovsky barriers was constructed on the basis NEB simulations for these sites, as shown in Fig. 4.3b. The crossing point of the Volmer and Heyrovsky activation energy lines occurs at or slightly below the range of energies which can be considered as the reference value of Pt(111)-catalyzed HER at 0.86 monolayer coverage. Notably, the crossing point for the corner sites in the 5-rings is shifted more toward thermoneutral adsorption energies than on the 6-ring. This suggests that such relatively low energy pathways are more accessible on the 5-ring structures since the crossing point resides within the range of observed hydrogen adsorption energies (= local hydrogen coverages) unlike on the 6-ring. Indeed, constructing Volmer-Heyrovsky reaction energy diagrams from the fitted activation and reaction energies reveals that the rate-determining step barriers for the 5-ring corner sites are very similar and lower than on the 6-ring for most equivalent hydrogen coverages, see representative example in Fig. 4.3c.

Contrasting these results to the barriers reported for pristine CNTs in Publication I and Refs. 9,183 indicates that the corner site in the 6-ring is insensitive to the nanotube termination and remains inactivate toward HER with a barrier larger than 1 eV. On the contrary, many sub-eV reaction pathways can be constructed for the 5-ring corner sites, even reaching values comparable to or below Pt(111). The results therefore demonstrate that the 5-ring corner sites should be notably more active toward HER than pristine CNT. Because the barriers on the 6-ring are identical on open-ended and pristine CNTs, edge termination cannot be the sole factor activating these 5-ring sites, which suggests that the performance improvement should also extend to 5-ring structures in other materials, such as fullerenes or defected nanotubes. Interestingly, the difference between the reactivity of 5-ring and 6-ring corner sites is not due to drastically smaller activation energies but due to a better balance between the energetics of the two reaction steps. It is also worth noting that the presented energy diagrams are, by construction, upper bounds because the hydrogen coverage is kept fixed during the reaction. Alternative pathways to filling the surface sites, which nevertheless lead to the same net reaction, can result in a rather significant reduction of the HER barrier, see example in Supporting Information of Publication II and the discussion of Ref. 183.

In order to elucidate the origins between the HER activities of 5- and 6-rings, an analogous model to the metal-catalyzed Schmickler model was derived by using localized bond orbitals. For each atomic site $j$, this model involves measuring the distance between the system’s localized HOMO (see Fig. 4.4a) and the occupancy $q_{i\sigma}$ weighed average orbital energy $\epsilon$ according to

$$
\Delta \epsilon_j = \epsilon_{\text{IBO}} - \frac{1}{\sum_{i,a} q_{i\sigma} \sum_{\sigma=\uparrow,\downarrow} \sum_i q_{i\sigma} \epsilon_{i\sigma}} \sum_{i,a} q_{i\sigma} \epsilon_{i\sigma} \tag{4.1}
$$

The site-type specific quantity was obtained by averaging over the computed $\Delta \epsilon_j$ values for all similar sites. These averaged orbital energies were then cor-
related with calculated kinetic barriers from NEB simulations, see Fig. 4.4b. Because experimental notions of catalytic activity do not enter into the model (via $\Delta G_{\text{ads}}^H$-based volcano plots), all problems related to the heterogeneity of carbon nanomaterials is avoided completely, which I argued in Sec. 2.1 was the biggest flaw of the similarly motivated DOS-based model proposed by Qiao and coworkers.\textsuperscript{58} Here, the orbitals were localized from the DFT Slater determinants using atom-centered Gaussians and the intrinsic bond orbital (IBO) method, which preserves chemically intuitive orbitals, e.g., delocalized $\pi$-bonds in conjugated compounds, but at the same time does not introduce any empirical bias to the localization procedure.\textsuperscript{186,187} The aforementioned analysis was performed at the low coverage limit where only the CNT edge is hydrogenated, as the determination of equivalent hydrogen coverages on different surface sites is not trivial. This coverage was, however, noted to be rather improbable since filling additional sites remains exothermic.

On the basis of Fig. 4.4b, the activity ordering of surface sites on the 5-ring terminated CNT correlates linearly with the $\Delta \epsilon_j$ descriptor, at least under the given hydrogen coverage conditions, with the catalytically most active corner sites exhibiting localized IBOs closest to the HOMO energy level. This result is in excellent agreement with proposed reactivity theories on metals where a $d$-band spanning the Fermi level was a vital prerequisite for efficient catalysis.\textsuperscript{43} The same main conclusion was reached in the DOS model of Qiao et al.\textsuperscript{58} on the basis of $\Delta G_{\text{ads}}^H$ calculations. The current results are also consistent with this model in the sense that an analysis of the DOS reveals that the corner sites (and other sites) introduce states directly at the Fermi level, though notably no trend between HER activation energies and $\Delta \epsilon_{\text{ads}}^H$ was observed, see Supporting Information of Publication II.

As the tube chirality is changed, the linear relationship between HER reactivity and $\Delta \epsilon_j$ essentially vanishes, although only two distinct sites were considered on the 6-ring terminated CNT. A clear difference between 5-ring and 6-ring corner sites is, nonetheless, obvious since only on the 6-ring the localized corner site orbitals reside deep below the HOMO level. This suggests ring strain.
plays a crucial role in differentiating the catalytic activities of different carbon sites. Unsatisfyingly, the same linear relationship does not appear to hold for different tube chiralities even when the difference in positions of the Fermi level is taken into account, reducing the global predictive power of $\Delta \epsilon_j$.

### 4.1.3 Electron Overdelocalization Effects

DFT simulations with PBE$^{158}$ and other GGA-level exchange-correlation functionals suffer from varying degrees of self-interaction error, which may lead to an overdelocalization of the electron density and spurious charge transfer effects, as was discussed in Sec. 3.3. This negatively affects the quality of DFT predicted activation and reaction energies needed in the construction of kinetic electrocatalysis models. Constrained DFT configuration interaction was adopted in Publication IV to assess the severity of these errors in the HER calculations of the open-ended CNTs considered in Publication II and described in Sec. 4.1.2.

CDFT-CI simulations require the definition of a suitable diabatic basis to represent the studied reaction. The Volmer-Heyrovsky mechanism is composed of two proton-coupled electron transfer reactions, which suggests that the diabatic theory proposed by Soudackov and Hammes-Schiffer$^{16,46,48}$ for completely generic PCET reactions is a prime candidate for defining the diabatic basis. The SHS theory was originally devised for reactions where, in general, the proton and electron are transferred between two distinct chemical groups and the direction of PT/ET need not be the same. The notable difference between this theoretical framework and the Volmer-Heyrovsky reactions considered herein is the fact that HER involves the reduction of protons to hydrogen atoms, which subsequently either bind to the catalyst surface (Volmer step) or form molecular hydrogen (Heyrovsky). Nevertheless, the theory can be adapted to the Volmer-Heyrovsky mechanism as will be demonstrated below.

The SHS theory extends the diabatic picture of electron transfer processes (see Sec. 3.4.2 and Ref. 49) by introducing two extra states in addition to the reactant and product states which represent the concerted transfer of a proton and an electron. These so-called off-diagonal states correspond to the intermediary configurations of sequential ET/PT or PT/ET mechanisms. Extending these notions to HER allows the definition of four diabatic states for the Volmer and Heyrovsky steps, see Fig 4.5a for the former case and the Supporting Information of Publication IV for the latter. Notably, the “sequential” pathway which is initiated by electron transfer must now be completed by a hydrogen atom transfer (HT) step, not proton transfer, simply because the proton is reduced to a hydrogen atom during the ET step. The reverse ordering of the HT/ET reactions completes the definition of the diabatic basis.

The diabatic states defined in Fig. 4.5a were constructed with fragment-based CDFT constraints as indicated in the figure and outlined in Sec. 3.4.1, further subdividing each state into two to account for explicit solvation effects, refer to Publication IV for the exact details. I wish to emphasize that the introduction
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IS:
- electron transfer
- proton coupled electron transfer
- hydrogen transfer

FS:
- electron transfer
- hydrogen transfer

HT:
- electron transfer
- hydrogen transfer

a) The diabatic states used as the basis for Volmer reaction CDFT-CI simulations. The diabatic states are constructed using fragment constraints by splitting the states into two fragments as indicated. These states do not represent stable observable configurations. b) Representative Volmer (b) and Heyrovsky (c) energy profiles from Publication II recalculated with CDFT-CI. The labeling is explained in the main text.

![Image of diabatic states and energy profiles](image)

**Figure 4.5.**

Prior to recalculating some of the Volmer-Heyrovsky minimum energy paths on open-ended CNTs, the CDFT-CI methodology was extensively tested with a simpler model system, see Publication IV. The accuracy of the implemented CDFT algorithms in CP2K was previously validated in Publication III as will be detailed in Sec. 4.2. Representative CDFT-CI energy profiles are compared to DFT results in Figs. 4.5b,c. The CDFT-CI results were evaluated with three alternate basis set definitions by expanding the adiabatic state either in terms of all four states from Fig. 4.5 (labeled 4 states), using just the reactant and product states (2 states), or by combining the diabats connected via ET into two effective states with block diagonalization (4 states, block).

The results of Fig. 4.5 demonstrate a notable difference between CDFT-CI and DFT using the PBE exchange-correlation functional. At least in the studied systems, the Volmer-Heyrovsky barriers are increased by 0.1 – 0.3 eV and the reaction energies decreased (more exothermic) by 0.1 – 0.2 eV as a consequence of the CDFT-CI treatment, depending on the considered reaction, active surface site, and hydrogen coverage conditions. The larger barriers are consistent with the findings of Van Voorhis and coworkers\(^{169}\) for gas phase chemical reactions.
The CDFT-CI adiabatic wavefunction can mostly be described as the linear combination of reactant and product diabatic states, as their combined weight exceeds over 95% in every system at each discrete image along the reaction coordinate. Nevertheless, slight differences in the predicted activation energies of the four and two state models are observed for some systems, stemming from the nonzero contribution of the diabat that represents the electron transfer intermediary. The off-diagonal states cannot thus be safely ignored to reduce computational cost on these grounds. The effects of the third, block diagonalized basis is difficult to analyze without further simulations as the transformation induces delicate modifications to the weights of each diabat; however, this approach might prove useful in the semiclassical vibronic adiabacity analysis of reactions defined in terms of multiple diabatic states, see short discussion in Publication IV and e.g. Ref. 48 for a more comprehensive account.

By construction, the disparities between CDFT-CI and DFT energy profiles must be the direct result of electron density differences. Two possible contributions may be identified: either the methods partition the electron density differently between the system’s components, i.e., water, CNT and the proton, or the degree of density delocalization is dissimilar. The lack of a ground state density for the CDFT-CI multiconfigurational wavefunction prevents a detailed analysis, but some qualitative trends may be extracted by simply inspecting the partial charges in the DFT ground state and the CDFT diabatic states. Referring to the details in Publication IV, such an analysis reveals that the CNT donates more electrons during the Volmer-Heyrovsky reaction according to CDFT-CI than DFT. Moreover, the use of density-localized diabatic states as the basis for constructing adiabatic states can be argued to be the cause of increased barriers with CDFT-CI. Although more extensive testing is required to elucidate the differences between DFT and CDFT-CI and to ensure convergence of the CDFT-CI diabatic basis, the discussed preliminary results suggest that CDFT-CI could be a computationally efficient tool toward more accurate kinetic models for HER and other electrocatalytic PCET reactions. It is also worth mentioning that the reaction MEPs could, in principle, be optimized directly at the CDFT-CI level, although the necessary nuclear gradients are quite cumbersome.

4.2 CDFT Applied to Homogeneous Electron Transfer

The core algorithms developed in this thesis, outlined in Sec. 3.4.3, to perform CDFT simulations within the hybrid Gaussian and planewaves framework in CP2K were validated in Publication III. Benchmark tests were performed by reproducing previously reported CDFT results for electron and hole transfer reactions in relatively small gas phase systems obtained with other computational codes. The focus of these tests mainly revolved around confirming that the implementation was able to reproduce the value of the electronic coupling $|H_{ab}|$ which, as defined in Sec. 3.4.2, measures the interaction strength between
CDFT diabatic states. High-level reference data from wavefunction methods are available for validation in these systems. Additionally, the use of the Becke density partitioning method together with fragment constraints was validated by computing charge transfer energies in strongly interacting bimolecular systems.

In summary, the aforementioned tests demonstrated that the implemented CDFT algorithm is as accurate as other CDFT implementations, which differ from the present method in their choice of numeric basis set to expand the Kohn-Sham orbitals, the algorithm to solve the CDFT eigenvalue equations, and the type of weight function used in defining the constraint potentials. Instead of focusing on these validation simulations, this section will discuss one prospective application of CDFT simulations to evaluate kinetic electron transfer parameters within the Marcus formalism. This is a stringent test of the method’s computational efficiency as will be demonstrated below. The organic mixed-valence compound tetrathiafulvalene-diquinone (Q-TTF-Q•−), shown in Fig. 4.6a, was considered as an example system due to the wide availability of reference data.

Performing condensed phase molecular dynamics simulations of large systems with DFT is one of the primary strengths of CP2K, see e.g. Ref. 129, which the underlying theoretical methods have made possible. Leveraging this capability for efficient MD-based characterizations of electron transfer kinetics was one of the main design criteria for the implemented CDFT algorithm. To concretely establish what steps such simulations involve, the Marcus ET framework is adopted where, according to Eq. (3.28), the rate constant depends on three parameters: \(|H_{ab}|, \lambda, \Delta G\). The latter two quantities may be evaluated by measuring the vertical energy gap between the reaction reactant (IS) and product (FS) diabatic states at fixed nuclear coordinates \(R^K\).

\[
\Delta E(R^K) = E_{\text{CDFT}}^{\text{FS}}(R^K) - E_{\text{CDFT}}^{\text{IS}}(R^K)
\] (4.2)

This quantity must be sampled from two sets of canonical molecular dynamics simulations and averaged appropriately, where the atoms are propagated with forces derived from the IS diabatic state in one simulation and from the FS diabat in the other. The definitions for \(\lambda\) and \(\Delta G\) simplify considerably in the case that the reactant and product states are symmetric, \(\lambda = \langle \Delta E \rangle_T\) and \(\Delta G = 0\), as is the case with Q-TTF-Q•−. These equations imply that only a single MD simulation on the potential energy surface of either diabatic state is necessary, though both states are naturally required to compute \(|H_{ab}|\) and \(\Delta E\).

Solving the energies, forces, and couplings \(|H_{ab}|\) between two diabatic states continuously during a condensed phase MD simulation at the full CDFT level (without hybrid QM/MM methods) is a formidable computational challenge because each time step requires performing two CDFT SCF energy optimizations. Prior approaches have avoided this issue by sampling \(|H_{ab}|\) and \(\Delta E\) less frequently, say every 50th time step. In practice, only one state is thus explicitly included in the MD simulation, while single-point computations are used to evaluate the ET quantities. By contrast, both CDFT states were treated...
Results and Discussion

in parallel during the MD simulations in Publication III by developing an algorithm which builds the Becke weight function $w_{c}(r)$ and its atomic gradients prior to starting SCF energy optimizations. When combined with extrapolation schemes for the CDFT Slater determinant and the Lagrange multipliers $\xi$,

excellent scaling to large processor counts was demonstrated, yielding an average performance of 48 s/time step on 384 cores for the Q-TTF-Q$^{-}$ system when averaged over a 24 000 step simulation, while load imbalance remained within reasonable limits. A serial mode algorithm to treat more heterogeneous sets of CDFT states and constraints was later implemented in Publication IV.

The time evolution of $\Delta E$ and $|H_{ab}|$ during the CDFT MD simulation of Q-TTF-Q$^{-}$ in 258 explicit water molecules are shown in Figs. 4.6b,c. By taking averages, the solvent reorganization energy was estimated as 130 mHa and the effective electronic coupling as 15.4 mHa with the PBE functional. Single-point calculations with the PBE0 hybrid from equispaced snapshots of the trajectory yield a notably smaller $|H_{ab}|$ of 3.0 mHa due to decreased overlap between the CDFT diabats. These estimates are not directly comparable with experimental values, $\lambda = 41$ mHa and $|H_{ab}| = 0.7$ mHa in 10:1 ethyl acetate/tert-butanol, because the compound precipitates in water.

The correspondence can nevertheless be considered satisfactory since the stronger hydration properties of water enable the better stabilization of the excess charge in water, leading to an increase in $\lambda$. Furthermore, the CDFT simulations were able to correctly predict that Q-TTF-Q$^{-}$ can be classified as a class II compound ($2|H_{ab}| < \lambda$) in the Robin-Day classification scheme for mixed-valence compounds, in agreement with the experimental results and another theoretical study. The inclusion of solvent molecules is crucial in computing $\Delta E$ and $|H_{ab}|$ for reaching this conclusion, as their omission can lead to the wrong prediction $2|H_{ab}| > \lambda$. 

Figure 4.6. a) Simulated Q-TTF-Q$^{-}$ system with 258 explicit water molecules. The localization of excess negative charge in the reactant (IS) and product (FS) diabatic states is indicated. b-c) Time evolution of the vertical energy gap (b) and the electronic coupling (c) during a CDFT MD simulation.
5. Conclusions and Outlook

One of the main objectives of this thesis was to review the theoretical challenges involved in the kinetic modeling of electrocatalytic reactions and to examine prospective solutions. Overall, this survey revealed that the quest toward more accurate models and, ultimately, the design of better performing catalysts is quite a demanding task, which will require addressing issues unique to electrochemical systems (Chap. 2) in addition to more general DFT-related limitations (Chap. 3). [Q1]

Building upon this foundation, a model for carbon nanotube-catalyzed hydrogen evolution was developed, striving to maintain a reasonable balance between accuracy and computational cost. Hydrogen coverage, solvation, and electrode potential were determined the most crucial variables to consider in the kinetic models of HER in order to reliably compare the reactivity of different surface sites. The effects of simple nanotube functionalizations on HER activity were subsequently evaluated with this model, serving as a good baseline for possible future studies employing more complex structural modifications. [Q2]

The impact of hydrogen coverage on the HER reactivity of CNTs was modeled with an approach where minimum energy path simulations were conducted using three distinct local coverages. Hydrogen adsorption energies were employed to distinguish different coverages, resulting in a roughly linear dependence between kinetic parameters and the adsorption energy. This method enables the construction of HER energy diagrams for any local hydrogen coverage, which was deemed a necessary strategy on CNTs because sites in the nanotube lattice exhibited strong neighbor-neighbor interactions, and because experiments are unable to provide a satisfactory reference coverage. The largest deficiencies of the proposed scheme are the assumptions of a static coverage and the inability to estimate the probability of observing a particular coverage at actual reaction conditions. Kinetic Monte Carlo simulations parametrized by more extensive barrier calculations could, in principle, be adopted to overcome these issues, however, this would impose a substantial increase in computational cost.

The developed kinetic model was able to correctly predict that HER proceeds via the Volmer-Heyrovsky mechanism on carbon nanotubes, with the latter step being the rate-limiting step as a consequence of its larger barrier. Furthermore,
the model unequivocally demonstrated why pristine CNTs are poor HER catalysts when compared to simulated results on Pt(111).\textsuperscript{8} Introducing a single substitutional nitrogen dopant did not result in the activation of the nearest carbon site, although the $\Delta G_{\text{ads}}^H$-based “volcano plot” descriptor model would have suggested otherwise. Experimental evidence indicating a converse effect due to nitrogen doping was argued to be the result of more complex atomic arrangements of nitrogen and carbon. By contrast, the formation of 5-ring structures on open-ended CNTs was discovered to lead to enhanced activity when contrasted to a 6-ring terminated CNT, even approaching the level of Pt(111). Ring strain was proposed to be the main cause for increased reactivity, suggesting that 5-rings in other carbon nanomaterials, e.g., fullerenes or defected CNTs, might intrinsically exhibit a better HER activity than conventional 6-rings.

In an effort to understand reactivity trends on functionalized nanotubes, the use of an orbital-dependent descriptor was explored on the open-ended CNTs to address the deficiencies of the $\Delta G_{\text{ads}}^H$ descriptor model. At the low coverage limit, HER activation energies linearly correlated with this descriptor on the 5-ring terminated CNT, demonstrating that the most active sites were those with valence orbitals closest to the Fermi level, in accordance with proposed theories on transition metals.\textsuperscript{43} Unfortunately, changing the tube chirality resulted in the disappearance of this trend which persisted even as the relative positions of the Fermi levels were taken into account. Further work is, therefore, clearly required to develop better transferable activity descriptors for carbon nanomaterials, ultimately facilitating screening studies of functionalized CNTs.

The effects of varying electrode potential were considered with a scheme based on the double reference method\textsuperscript{96,97} where kinetic simulations were repeated with several system net charges. Potential alignment and energy corrections were applied to obtain constant Fermi level (grand canonical) reaction and activation energies as a function of the electrode potential. On a semiquantitative level, the results from this model were fully reasonable as HER activity increased the larger the applied overpotential. Although contrasting NCNT with CNT was unaffected by methodological limitations, fully rigorous comparisons to different systems and other potential correction schemes were hindered by the presence of a compensating uniform background charge in the employed scheme. This deficiency should be addressed in future studies by adopting an alternative charge compensation scheme, e.g., the combined implicit solvation and jellium model.\textsuperscript{89} Another step toward better accuracy would be to maintain constant Fermi level self-consistently, thus better mimicking actual electrocatalytic conditions.\textsuperscript{81,84,89,92} Such approaches will naturally impose an increase in computational cost and would benefit from further algorithmic developments.

Resolving the limitations of DFT is integral in the development of more accurate electrocatalytic models. The electron self-interaction error was identified as a major source of imprecision that reduces the predictive power of DFT-based kinetic models. CDFT-CI simulations combined with charge-localized diabatic electronic states were leveraged to critically investigate the impact of SIE on the
Conclusions and Outlook

A set of four diabatic states was associated with both elementary steps of the Volmer-Heyrovsky mechanism by adapting the Soudackov–Hammes-Schiffer\textsuperscript{16,46} theory of proton-coupled electron transfer, an approach that should generalize to other electrocatalytic PCET reactions. Density constraints were imposed on the system in order to construct the diabatic states using a CDFT framework implemented in this thesis in the CP2K\textsuperscript{143,144} software. A comparison of CDFT-CI and DFT simulations at the PBE level indicated that standard DFT underestimates activation energies by 0.1–0.3 eV and overestimates reaction energies by 0.1–0.2 eV. These observations were rationalized by the reduction of electron density delocalization and the prevention of excessive charge rearrangement phenomena as a consequence of the CDFT-CI treatment.\textsuperscript{169}

All in all, the results from CDFT-CI simulations demonstrated that the method could be a prime candidate toward more accurate kinetic models of HER and other electrocatalytic reactions when combined with a suitable diabatic basis. However, a more extensive comparative study of DFT and CDFT-CI is first required. Such comparisons would benefit from the development of a tool to measure differences between the DFT ground state density and the CDFT-CI multiconfigurational Slater determinant. A second aspect that would aid in this effort would be the construction of a benchmark database for electrocatalytic reactions, which would also enable systematic comparisons of DFT with other theoretical approaches. Ideally, this database would be comprised of both simpler nonperiodic gas phase systems and extended surface systems.\textsuperscript{198,199} Other methods for producing diabatic states, e.g., multistate DFT,\textsuperscript{200} should also be contrasted with CDFT-CI.

Another appealing future research avenue is the wider adaptation of the SHS PCET theory, which was utilized in this thesis only to define the diabatic states for CDFT-CI. This framework is, however, more versatile than adopted herein, as was briefly explored in Chap. 3. In particular, two research directions that could advance the fundamental understanding of HER electrocatalysis is the exploration of vibronic diabatic effects and the combination of SHS theory with grand canonical DFT. This strategy could be a powerful complementary approach to conventional methods for estimating HER kinetics.

In conclusion, this thesis has examined the unique challenges involved in electronic structure simulations of electrocatalytic reactions from the perspective of nanotube-catalyzed hydrogen evolution, which range from fundamental theoretical limitations to more practical problems related to computational tractability aspects. An attempt to summarize these issues was made so that future studies would be less fazed by the daunting number of methods proposed to tackle them. Despite the plethora of unresolved challenges highlighted in this work, I remain confident that none of them is insurmountable in the long term with persevering research, ultimately deepening our understanding of electrocatalysis and enabling the tailoring of better catalysts.
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The hydrogen evolution reaction is a sustainable process to produce hydrogen from water using electricity. Hydrogen is a zero-emission fuel that has the potential to replace petroleum in transportation applications. The cost of electrochemical hydrogen production remains high in part due to the use of scarce noble metals as catalysts. Functionalized carbon nanotubes are an appealing class of materials toward cheaper hydrogen evolution catalysis.

Density functional theory simulations enable the study of reaction kinetics at the atomic level. They can provide valuable insight into the origins of catalytic activity and help to explain why certain catalyst modifications improve performance more than others.

In this thesis, a computational model was developed for the hydrogen evolution reaction on carbon nanotubes. The impact of simple nanotube functionalizations was considered, laying the foundations for future studies using more complex carbon-based catalysts.