Jonathan E. Mueller, Donato Fantauzzi, and Timo Jacob

1.1 Introduction

As one of the classic branches of physical chemistry, electrochemistry enjoys a long history. Its relevance and vitality remain unabated as it not only finds numerous applications in traditional industries, but also provides the scientific impetus for a plethora of emerging technologies. Nevertheless, in spite of its venerability and the ubiquity of its applications, many of the fundamental processes, underlying some of the most basic electrochemical phenomena, are only now being brought to light.

Electrochemistry is concerned with the interconversion of electrical and chemical energy. This interconversion is facilitated by transferring an electron between two species involved in a chemical reaction, such that the chemical energy associated with the chemical reaction is converted into the electrical energy associated with transferring the electron from one species to the other. Taking advantage of the electrical energy associated with this electron transfer for experimental or technological purposes requires separating the complementary oxidation and reduction reactions of which every electron transfer is composed. Thus, an electrochemical system includes an electron conducting phase (a metal or semiconductor), an ion conducting phase (typically an electrolyte, with a selectively permeable barrier to provide the requisite chemical separation), and the interfaces between these phases at which the oxidation and reduction reactions take place.

Thus, the fundamental properties of an electrochemical system are the electric potentials across each phase and interface, the charge transport rates across the conducting phases, and the chemical concentrations and reaction rates at the oxidation and reduction interfaces. Traditional experimental techniques (e.g., cyclic voltammetry) measure one or more of these continuous observables in an effort to understand the interrelationships between purely electrochemical phenomena (e.g., electrode potential, current density). While these techniques often shed light on both fundamental (e.g., ionic charge) and statistical (e.g., diffusion rates) properties of the atoms and ions that make up an electrochemical system, they provide little insight into the detailed atomic structure of the system.

In contrast, modern surface science techniques (e.g., STM, XPS, SIMS, LEISS) typically probe the atomistic details of the interface regions, and support efforts to gain insight into the atomistic processes underlying electrochemical phenomena. Indeed, these methods have been applied to gas–solid interfaces with resounding success, elucidating the atomistic structures underlying macroscopic phenomena [1]. Unfortunately, the presence of the electrolyte at the electrode surface hampers the application of many of these surface science techniques. Because the resulting solid–electrolyte interface is an essential component of any electrochemical system, electrochemistry has not yet fully experienced the atomistic revolution enjoyed by other departments of surface science, although these techniques are increasingly making their way into electrochemistry [2].

The dramatic increases in computing power realized over the past decades coupled with improved algorithms and methodologies have enabled theorists to develop reliable, atomistic-level descriptions of surface structures and processes [3]. In particular, periodic density functional theory (DFT) now exhibits a degree of efficiency and accuracy which allows it not only to be used to explain, but also to predict experimental results, allowing theory to take a proactive, or even leading, role in surface science investigations. A prime example of this is the design of a new steam reforming catalyst based on a combination of theoretical and experimental fundamental research [4].

The application of DFT to electrochemical systems is not as straightforward as it is to the surface–vacuum interfaces of surface sciences. There have indeed been promising efforts in this direction [5–7], and there is a growing interest in theorectical electrochemistry [8–10]; however, proper treatments of the electrolyte and electrode potential provide novel challenges for which there are not yet universally agreed upon solutions. Nevertheless, there are already success stories, such as the theoretical prediction [11,12] and experimental confirmation [13] of the nonmonotonic dependence of the electrocatalytic activity of the hydrogen evolution reaction (HER) on the thickness of Pd overlayers on Au(111).

Common to both the experimental and theoretical approaches mentioned above is the existence of two regimes – the macroscopic and the atomistic – and the importance of relating these in order to obtain a comprehensive picture of an electrochemical system. Statistical mechanics provides the necessary framework for relating the discrete properties and atomistic structures of the atomistic regime to the continuous variable controlled or observed in the macroscopic regime. The fundamental assumption underlying this relationship is what Richard Feynman called the "atomic hypothesis", which we rephrase in terms of electrochemistry as follows: "there is nothing that *electrochemical* systems do that cannot be understood from the point of view that they are made up of atoms acting according to the laws of physics" [14].

Modern computational methods, based on the principles of quantum mechanics, provide a means of probing the atomistic details of electrochemical systems, as do the techniques of modern surface science techniques. The concepts of statistical mechanics are critical for extending the results of these molecular scale models to macro-scale descriptions of electrochemical systems. Such a procedure creates a multiscale model of an electrochemical system, built up from the atomistic details of the quantum regime to a description of the electrochemical phenomena observed in macroscopic systems.

This chapter is intended to serve as an introduction to multiscale modeling for electrochemists with minimal background in the methods of modern computational chemistry. Thus, the fundamentals of some of the most important methods are presented within the framework of multiscale modeling, which integrates diverse methods into a single multiscale model, which then spans a wider range of time and length scales than is otherwise possible. The physical ideas underlying the methods and the conceptual framework used to weave them together are emphasized over the specific how-to details of running simulations. Thus Section 1.2 gives an overview of the multiscale modeling and Sections 1.3-1.5 present three different levels of theory used as components in many multiscale models: electronic structure modeling methods, molecular modeling methods, and chemical reaction modeling methods. The development of appropriate models for simulating electrochemical systems at each level of theory is the key outcome of each of these sections. To illustrate the application of some of the methods of multiscale modeling to electrochemistry, two concrete examples are presented in detail. In Section 1.6 a detailed mechanistic study of the oxygen reduction reaction on Pt(111) is presented. In Section 1.7 a similar study of formic acid oxidation illustrates additional approaches and modeling techniques. In both cases the focus is on the methods and modeling techniques used rather than the particular conclusions reached in each study.

1.2 Introduction to Multiscale Modeling

Electrochemical phenomena can be viewed over a wide range of time and length scales, ranging from electronic transfer processes which take place over distances on the scale of nanometers in times of the order of femtoseconds, to large-scale industrial processes involving moles of atoms occupying spaces best measured in meters and lasting hours, days or even years. Bridging these time and length scales is one of the central tasks of modern theoretical electrochemistry. This is the case for both scientists seeking to further our fundamental understanding of electrochemistry, and engineers developing applications of electrochemical processes and systems. Thus, the former continue the hard work of uncovering the atomistic processes underlying macroscopic electrochemical processes [2], while the latter seek to bring together interconnected phenomena spanning many time and length scales to design a product with the desired functionality [15]. In both cases a multiscale framework is needed to interrelate phenomena at the relevant time and length scales.

Traditionally, computational chemistry uses a single computational tool to model a given system at a particular time and length scale. Several of the major categories that these computational tools fit into, along with the approximate time and length scales, to which they can be applied, are shown in Figure 1.1. The physical laws appropriate for the system components or building blocks at each time and length scale govern the models developed at that level and determine which system



Figure 1.1 Schematic representation of various categories of simulation methods used in multiscale modeling according to the time and length scales of the models to which they are most applicable.

properties we can obtain directly. Thus each level of theory focuses on the system under a single aspect. Multiscale modeling aims at stitching these various aspects together into a unified whole, such that macroscopic properties emerge from underlying microscopic phenomena.

Two strategies are available for stitching methods of differing scales together into a single, coherent multiscale model. In the first, known as concurrent coupling, the various levels of simulation are incorporated into a single multiscale model. Thus, as illustrated in Figure 1.2, a single simulation makes direct use of various levels of theory and explicitly describes phenomena taking place at a range of time and length scales. Concurrent coupling is typically realized by dividing the system into various regions, each of which is treated using a different level of theory. Defining the boundaries between these regions and then determining how the regions interact with each other is the primary challenge in concurrent coupling. The key disadvantage, is that, because the time propagation of the system dynamics is limited by the process with the smallest time step, there are often only limited gains in the time scales which can be achieved using concurrent coupling schemes. Nevertheless, significant gains in the length scales treated are very realizable. A common example of concurrent coupling is QM/MM modeling in which an electronic structure method is used to describe a small reactive portion of a system, which is otherwise described using a molecular force field. We discuss this approach in greater detail in Section 1.4.3.3.

The second strategy, known as sequential coupling, uses results from modeling at one level as the inputs for a model at another level. This often entails fitting the parameters that define a model at one level to results derived from another level, and



Figure 1.2 Schematic representation of (a) concurrent and (b) serial coupling approaches to integrating two diverse levels of theory into a single, multiscale modeling framework. In concurrent coupling different parts of a single model system are treated using methods describing the system at two different levels of detail. Here a small region treated with a more detailed method (A) is typically embedded within a larger region described using a more course-grained method (B). The shaded overlap

region where the fibers from these distinct computational methods are woven together into a single, continuous model is critical to the successful implementation of a concurrent coupling approach. In serial coupling results obtained using a more fundamental method (A) are used as the basis for optimizing the parameters needed to define a course-grained method (B), which can then be applied to larger model systems for larger time and length scale simulations.

is often referred to as parameter passing. Thus, as shown in Figure 1.2, one method is derived from another, such that subsequent simulations carried out using the derived method are not constrained by the time and length scale limitations of the parent model(s). The aim in this procedure is often to extend the atomistic details, and thus presumably accuracy, of smaller scale methods to systems which would normally be too large for them to treat. Of course, there is a price to be paid for these gains in computational efficiency. Larger scale methods can only be derived from smaller (typically more exact) methods by making approximations and simplifying assumptions. To verify the validity of these approximations, it is important to make a direct comparison between results from the derived method and results from its parent method(s) for cases which were not included in the derivation. It is also possible that errors are propagated from the parent method(s) in the process of derivation. Comparison with experiment, where possible, is an important means of locating such errors. A common example of sequential modeling is force field parameter development and parameter optimization using results obtained from electronic structure calculations. This strategy is described in greater detail in Section 1.4.2.

Thus, communication between various levels of theory is at the heart of multiscale modeling. In the case of concurrent coupling this involves the continuous translation and shuttling of information across the boundaries between regions modeled using different methods in order to maintain the unity of the overall model. In the case of sequential coupling, information is first transferred from a parent to a daughter method, as the former method is derived or parametrized from the latter. However, subsequent validation requires the reverse flow of information as results from the derived method are returned to the parent method for comparison.

1.3

Electronic Structure Modeling

Multiscale modeling in electrochemistry typically begins at the atomic level, where the interactions of the electrons and nuclei which make up the electrochemical system are described in the language of quantum mechanics. Indeed, modern physics claims that the quantum mechanical description of such a system, in the form of a space- and time-dependent wave function, $\Psi(\mathbf{r}, t)$, is exact, and contains all that there is to know about the system. However, we are unable to obtain exact wavefunctions for all but the most trivial systems. Thus, Paul Dirac once famously noted: "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation" [16].

For several decades Dirac's prescription to avoid excessive computation was necessary for making headway in the effort to understand chemistry from quantum mechanical, first principles, and primarily conceptual rather than strictly numerical connections between quantum mechanics and chemical phenomena were developed. However, since the advent of modern computers and the subsequent exponential increase in their computing power, a new avenue for applications of quantum mechanics to chemistry has opened up which takes advantage of the enormous computing power available today.

1.3.1

Modern Electronic Structure Theory

Even with all of the computational resources available today, exact solutions to the Schrödinger equation are, in all but the simplest cases, unattainable. Thus, much effort has been dedicated to developing numerical methods for obtaining approximate wavefunctions that provide reliable descriptions of systems of interest. The aim of this section is to briefly present the conceptual underpinnings of modern electronic structure theory and methods and the conceptual bridges that can be used to link their results to macroscopic electrochemical systems. More detailed and complete treatments of quantum mechanics [14–18], quantum chemistry [19–21], statistical mechanics [22,23], chemical kinetics [24] and electronic structure methods [25–27] are readily available in many of the works referenced in this chapter, as well as in many more we have not had occasion to cite.

1.3.1.1 Quantum Mechanical Foundations

The central premise of quantum mechanics is that every physical system is completely described by a wavefunction, $\Psi(\mathbf{r}, t)$, such that all system properties can be obtained by consulting the wavefunction. [One must bear in mind that the wavefunction, $\Psi(\mathbf{r}, t)$, is defined over the configuration space of the system, rather than over three-dimensional space. In the following, we shall take \mathbf{r} to denote a point (or state of the system) in this configuration space.] Because the absolute square of the wavefunction, $\Psi(\mathbf{r}, t) \cdot \Psi^*(\mathbf{r}, t)$, in a region of configuration space is proportional to the probability

density of finding the system in the same region of space (or equivalently, in the state corresponding to that region of configuration space), the wavefunction of a system must be normalizable. Furthermore, physically meaningful wavefunctions are finite, single-valued, continuous and continuously differentiable over all space.

Operators (e.g., \hat{A}) and their corresponding eigenvalues (α_i) take the place of the dynamical variables used in classical mechanics. The eigenfunction solutions, ϕ_i s, of the corresponding eigenvalue equation:

$$A\phi_i = \alpha_i \phi_i \tag{1.1}$$

form a possible basis set for expressing the system states, which are represented as wavefunctions, $\Psi = \sum_{i} c_i \phi_i$. A single measurement on any state of the system always yields a single eigenvalue (α_i). The probability that a particular eigenstate is observed is proportional to the absolute square of its coefficient, c_i^2 , in the linear combination of eigenfunctions making up the initial state of the system, $\Psi(\mathbf{r}, t)$. However, once a particular eigenvalue, α_i , is observed the system remains in the corresponding eigenstate, ϕ_i , until it is further perturbed.

A collection of measurements on an ensemble of systems or particles with identical initial wavefunctions, results in an average value, that is, the expectation value $(\langle \hat{A} \rangle)$ of the system.

$$\langle \hat{A} \rangle = \int \Psi^*(\mathbf{r}, t) \hat{A} \Psi(\mathbf{r}, t) d\mathbf{r} = \int \Psi^*(\mathbf{r}, t) \hat{A} \Psi(\mathbf{r}, t) d\mathbf{r} = \sum_i \sum_j \alpha_i c_i c_j \int \phi_j^* \phi_i d\mathbf{r} = \sum_i \alpha_i c_i^2$$
 (1.2)

The dynamics of a non-relativistic, quantum mechanical system are governed by the time-dependent Schrödinger equation:

$$i\hbar\left(\frac{\partial\Psi(\mathbf{r},t)}{\partial t}\right) = \hat{H}\Psi(\mathbf{r},t)$$
(1.3)

When the energy of the system (i.e., \hat{H}) has no explicit time dependence, we can derive and make use of the time-independent Schrödinger equation:

 $\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \tag{1.4}$

The Hamiltonian operator, \hat{H} , which operates on the wavefunction to extract the system energy, *E*, contains both potential energy terms for the interactions of particles in the system with each other or any external fields, \hat{V} , and a kinetic energy term, \hat{T} , for each particle, which for a particle with mass *m* is written in atomic units¹⁾ as:

$$\hat{T} = \frac{-\nabla^2}{2m} \tag{1.5}$$

 Atomic units simplify the appearance of many of the most important equations in quantum mechanics by setting the following constants as fundamental atomic units equal to 1: the unit of mass is the rest mass of an electron (m_e = 1 atomic unit of mass), the unit of charge is the elementary charge (e = 1 atomic unit of charge), the unit of angular momentum is the reduced Planck's constant ($\hbar = 1$ atomic unit of angular momentum), the atomic unit for the electric constant is the Coulomb force constant ($\frac{1}{4\pi e} = 1$ atomic unit). Atomic units for other dimensions are readily derived from these.

For a molecule composed of *N* nuclei with nuclear masses and charges m_v and Z_v , respectively, and *M* electrons, \hat{H} can be written as:

$$\hat{H} = \sum_{\nu=1}^{N} \frac{-\nabla_{\nu}^{2}}{2m_{\nu}} + \sum_{i=1}^{M} \frac{-\nabla_{i}^{2}}{2} - \sum_{i=1}^{M} \sum_{\nu=1}^{N} \frac{Z_{\nu}}{|\mathbf{r}_{i} - \mathbf{R}_{\nu}|} + \frac{1}{2} \sum_{\substack{i,j=1\\i\neq j}}^{M} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} + \frac{1}{2} \sum_{\substack{\nu,\mu=1\\\nu\neq\mu}}^{N} \frac{Z_{\nu}Z_{\mu}}{|\mathbf{R}_{\nu} - \mathbf{R}_{\mu}|} = \sum_{\nu=1}^{N} \hat{T}_{\nu} + \sum_{i=1}^{M} \hat{T}_{i} + \hat{V}$$

$$(1.6)$$

The form of the potential energy terms describing the electromagnetic interactions between each pair of particles couples the motions of the particles, barring analytical solutions for all but the most trivial systems. Nevertheless, useful approximate solutions are within reach for many systems of interest, in part due to the variational principle, which states that because all solutions of the Schrödinger equation are linear combinations of the eigenfunction solutions, that the ground state (i.e., lowest energy) solution forms the lower limit of the system energy. Thus, the energy of any solution we generate will be greater than or equal to the ground state energy, and we can optimize any approximation of the ground state by minimizing its energy.

1.3.1.2 Born–Oppenheimer Approximation

The Hamiltonian for a molecule includes kinetic and potential energy terms for both electrons and nuclei, and operates on a wavefunction describing both electrons and nuclei. However, because the kinetic energy of the nuclei is small relative to the electronic kinetic energy, it can be ignored. This allows the electronic wavefunction to be calculated based on localized nuclear coordinates, rather than a delocalized nuclear wavefunction. Thus, the following electronic Schrödinger equation can be separated out of the time-independent Schrödinger equation:

$$\begin{split} \hat{H}_{e}\Psi_{e}(\mathbf{r}_{i}, \{\mathbf{R}_{\nu}\}) \\ &= \left(-\sum_{i=1}^{M} \frac{1}{2} \nabla_{i}^{2} + \frac{1}{2} \sum_{\substack{i,j=1\\i\neq j}}^{M} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} - \sum_{i=1}^{M} \sum_{\nu=1}^{N} \frac{Z_{\nu}}{|\mathbf{r}_{i} - \mathbf{R}_{\nu}|}\right) \Psi_{e}(\mathbf{r}_{i}, \{\mathbf{R}_{\nu}\}) \quad (1.7) \\ &= E_{e}(\mathbf{R}_{\nu})\Psi_{e}(\mathbf{r}_{i}, \{\mathbf{R}_{\nu}\}) \end{split}$$

where $\Psi_{e}(\mathbf{r}_{i}\sigma_{i}, \{\mathbf{R}_{\nu}\})$ are the electronic wave functions, and $\{\mathbf{R}_{\nu}\}$ denotes that nuclear spatial coordinates are parameters and not variables.

In this approximation, first introduced by Max Born and J. Robert Oppenheimer in 1927 [28], the heavy nuclei are thought of as fixed relative to the rapid motion of the quickly moving electrons, allowing the electrons to fully equilibrate to fixed nuclear positions. The equilibrated electronic energy as a function of the nuclear coordinates then forms a potential energy surface, with local minima (stable structures) and saddle points (transition states). Thus, obtaining the electronic structure and the corresponding system energy as a function of the nuclear positions is important in computational chemistry. The Born–Oppenheimer approximation is appropriate for the vast majority of cases; however, it breaks down for nuclear configurations where there are solutions to the electronic Schrödinger equation with similar energies.

1.3.1.3 Single-Electron Hamiltonians

While the Born–Oppenheimer approximation simplifies the Schrödinger equation by separating out the motion of the nuclei, the wavefunctions for the electrons are still coupled through their electrostatic interactions, making the resulting equations very difficult to solve. Of course there is no such difficulty for a single-electron system.

$$\left[\frac{-\nabla^2}{2} + \sum_{\nu=1}^N \frac{-Z_{\nu}}{|\mathbf{r} - \mathbf{R}_{\nu}|}\right] \psi_e = E_e \psi_e \tag{1.8}$$

This suggests that a crude, but readily soluble, approximation for a multi-electron system might be made by neglecting the electron–electron interactions altogether, so that the wavefunction for each electron ψ_i is solved for independently.²⁾ In this case, the total electronic wavefunction, Ψ_e , would be written as the product of single electron wavefunctions ψ_a . The total wavefunction is known as the Hartree product:

$$\Psi_{\rm e} = \prod_{i,j} \psi_i(\mathbf{r}_j) \tag{1.9}$$

A more reasonable approximation than non-interacting electrons is to decouple the motions of the electrons, so that each electron interacts with the field associated with the average charge density of the other electrons rather than directly with the wavefunctions describing the other electrons. The resulting single-electron hamiltonian is known as the Hartree hamiltonian [29–31] (here for the *i*th-electron):

$$h_{i} = -\frac{\nabla_{i}^{2}}{2} + \sum_{\nu=1}^{N} \frac{-Z_{\nu}}{|\mathbf{r}_{i} - \mathbf{R}_{\nu}|} + \sum_{j=1}^{M} \int \psi_{j}^{*}(\mathbf{r}') \frac{1}{|\mathbf{r}_{i} - \mathbf{r}'|} \psi_{j}(\mathbf{r}') d\mathbf{r}'$$
(1.10)

Because the final potential energy term contains the charge density of the other electrons, the electronic wavefunctions are now dependent on each other. Thus, to evaluate the Hartree hamiltonian for one electron, the wavefunctions for all of the other electrons (or at least their net charge density distribution) must first be known. The way out of this chicken and egg problem, is to start with a trial wavefunction. This initial guess provides the background charge density for solving for each singleelectron Hartree hamiltonian individually. These new solutions then provide the initial guess for a new set of solutions. The process can be repeated iteratively until the solutions converge (i.e., the wavefunctions remain relatively unchanged over the

²⁾ Here we use ψ instead of Ψ to indicate single-particle wavefunctions of a multi-particle system.

course of a single iteration in which each wavefunction is optimized against the other current wavefunctions in turn) in what is known as a self-consistent field (SCF) method. The energy for such a system can be written as the sum of the energies of the single-electron hamiltonians; however, because each electron–electron interaction is fully accounted for twice (i.e., once in the single electron hamiltonian of each electron involved) we must compensate for the double counting by subtracting the total electron repulsion energy from the sum of individual electron energies. Thus, the total energy of the system can be written as:

$$E = \sum_{i=1}^{M} \varepsilon_i - \frac{1}{2} \sum_{j \neq i} \iint \frac{\rho_i \rho_j}{\mathbf{r}_{ij}} \mathrm{d}^3 \mathbf{r}_i \mathrm{d}^3 \mathbf{r}_j$$
(1.11)

where ρ_i is the self-consistent charge density distribution corresponding to the single-electron wavefunctions, $\psi_i(\mathbf{r}_i)$.

1.3.1.4 Basis Sets

The single-electron wavefunctions (ψ_i) that form the Hartree product total electronic wavefunctions are not known analytically, but rather must be formed from some other basis set (ϕ_β).

$$\psi_i = \sum_{\beta} c_{\beta} \phi_{\beta} \tag{1.12}$$

While, from a purely mathematical point of view, any complete, and thus infinite, basis set will do, in practice we are limited to finite basis sets. Furthermore, computational considerations favor small basis sets, whose functions, when substituted into the various HF equations, result in integrals which can be efficiently computed. At the same time, the resulting single-electron wavefunctions should be as accurate as possible. This is best accomplished by choosing basis functions that resemble the well-known solutions to atomic hydrogen.

1.3.1.4.1 **Slater and Gaussian Type Orbitals** An obvious choice along these lines is Slater type orbitals [32] (STOs), centered on the atomic nuclei. This basis set mirrors the exact orbitals for the hydrogen atom, and naturally forms a minimum basis set, which means that each electron is described by only one basis function.

$$\Phi_{z,n,l,m}(r,\Theta,\phi) = NY_{l,m}(\Theta,\phi)r^{n-1}\exp(-Zr)$$
(1.13)

Unfortunately, all of the requisite integrals cannot be evaluated analytically, thus Gaussian type orbitals [33,34] (GTOs) provide an alternative basis, with easy to evaluate integrals.

$$\Phi_{z,n,l,m}(r,\Theta,\phi) = NY_{l,m}(\Theta,\phi)r^{2n-2-l}\exp(-Zr^2)$$
(1.14)

However, GTOs lack a cusp at the origin and decay too rapidly as they move away from the origin. This second deficiency can be remedied by using a linear combination of GTOs in place of each STO, which has been fit to reproduce the STO it replaces. Linear combinations of three GTOs have been found to optimize the relationship between accuracy and computational expense. This is known as the STO-3G basis set. Results can be further improved by moving beyond a minimum basis set, so that each electron orbital is described by not just one basis set orbital, but two, three or more. Such decompression results in so called double- ζ , triple- ζ , *and so on* basis sets. Additionally, polarization functions, consisting of basis functions with one quantum number higher angular momentum (i.e., p for s and d for p orbitals), can be included to give more flexibility to valence electrons, and diffuse functions included to better describe weakly bound electrons.

1.3.1.4.2 Plane Waves For periodic systems, particularly those with delocalized electrons, such as metals, plane waves provide a natural choice for the basis set:

$$\phi_{\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{-\mathrm{i}\mathbf{k}\mathbf{r}} \tag{1.15}$$

where for a unit cell vector **r**, **k** is restricted to the first Brillouin zone:

$$\mathbf{r} \cdot \mathbf{k} = 2\pi n \tag{1.16}$$

for *n* is any integer.

The size of the basis set required for the calculations to converge (i.e., the highest value of n) must be tested for each system.

1.3.1.4.3 Effective Core Potentials A common strategy for reducing the expense of modeling heavy elements, which contain many electrons, is to replace each nucleus and its core electrons with an effective core potential (ECP). The valence electrons, which are primarily responsible for chemical interactions, are then explicitly modeled in the presence of the ECP (or pseudopotential as it is called in the physics community). Besides reducing computational expenses, ECPs also provide a means of implicitly incorporating the relativistic effects which can be important for accurately describing the core electrons of heavy elements into a simulation without further complicating the rest of the treatment of valence electrons with unimportant relativistic contributions. While it is possible to include all core electrons in the ECP, better results are often obtained by modeling some of the highest energy core electrons explicitly alongside the valence electrons.

1.3.1.5 Enforcing the Pauli Principle

As fermions, electrons are not allowed to share identical states; rather, they are indistinguishable particles which must occupy distinct states in such a way that the sign of their combined wavefunction is reversed when they are exchanged. The Pauli principle requires that the total electronic wavefunction is antisymmetric with respect to the interchange of any two electrons. This implies two conditions. The first is that all single-electron spatial orbitals must be orthonormal:

$$\int \phi_i^* \phi_j \mathrm{d}r = \delta_{ij} \tag{1.17}$$

The second is that the overall wavefunction, $\Psi(..., i, ..., j, ...)$, is antisymmetric with respect to the exchange of any two electrons *i* and *j*:

$$\Psi(\dots,j,\dots,i,\dots) = -\Psi(\dots,i,\dots,j,\dots)$$
(1.18)

These rules are typically enforced by writing the total wavefunction in the form of a Slater determinant, whose terms are products of single-electron spin orbitals, $\psi_i = \phi_i \sigma_i$, which are each composed of a spatial orbital, ϕ_i , and a spin component, σ_i . For an *M*-electron system the Slater determinant has the following form:

$$\Psi_{e} = \frac{1}{\sqrt{M!}} \begin{vmatrix} \psi_{1}(\mathbf{r}_{1}\sigma_{1}) & \psi_{1}(\mathbf{r}_{2}\sigma_{2}) & \dots & \psi_{1}(\mathbf{r}_{M}\sigma_{M}) \\ \psi_{2}(\mathbf{r}_{1}\sigma_{1}) & \psi_{2}(\mathbf{r}_{2}\sigma_{2}) & \dots & \psi_{2}(\mathbf{r}_{M}\sigma_{M}) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{M}(\mathbf{r}_{1}\sigma_{1}) & \psi_{M}(\mathbf{r}_{2}\sigma_{2}) & \dots & \psi_{M}(\mathbf{r}_{M}\sigma_{M}) \end{vmatrix}.$$
(1.19)

Because electrons are indistinguishable, every electron appears in every orbital. Furthermore, electrons have two spin possibilities. Thus for every spatially distinct single-electron wavefunction there are actually a pair of orbitals, one with up (α) and one with down (β) spin. An appropriately anti-symmetrized pair of spin orbitals (α and β) have the form:

$$\frac{a(1)\beta(2) - a(2)\beta(1)}{\sqrt{2}}$$
(1.20)

1.3.1.6 Electron Correlation Methods

An important property of spin is that when the interaction of two same-spin orbitals is evaluated, an extra electron correlation, known as exchange, appears, due to the ability of same-spin electrons to avoid each other. Thus the expression for the potential energy of interaction between two same-spin electrons occupying orbitals ψ_i and ψ_i is:

$$V_{ee} = \iint \left(\frac{\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)\psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)\psi_i^*(\mathbf{r}_2)\psi_j^*(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) d^3r_1 d^3r_2$$
(1.21)
= $J_{ij} - K_{ij}$

While for opposite-spin electrons, it is simply:

$$V_{\rm ee} = \iint \frac{\psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2)\psi_i^*(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3r_1 d^3r_2 = J_{ij}$$
(1.22)

Nevertheless, this electron exchange is the only electron correlation accounted for in the Hartree–Fock method. Accounting for dynamical correlation due to explicit electron–electron interaction and non-dynamical correlation due to wavefunction contributions from higher energy electron configurations requires more advanced methods.

The Hartree–Fock equations approximate the Schrödinger equation by ignoring all correlation, with the exception of exchange. Nevertheless, by reintroducing this ignored electron correlation, they can be used as a stepping stone for returning to the full Schrödinger equation. How the Hartree–Fock method can be corrected to recapture the electron correlation that has been lost, is the subject of this section.

1.3.1.6.1 Configuration Interaction By solving the Hartree–Fock equations we arrive at an optimal HF wavefunction, Ψ_{HF} . Furthermore, we are also able to solve for excited states of the system, within the Hartree–Fock approximation, $\Psi_{\rm HF}^n$. Any one of these solutions can be substituted into the exact Schrödinger equation (i.e., operated on using the exact many-electron Hamiltonian operator to yield the system energy), such that the variational principle still applies. However, further improving any one of these solutions is hampered by the coupling of the electronic motions, which is the original problem the HF equations were designed to avoid. Nevertheless, if a set of Hartree–Fock configurations $\{\Psi_{\mathrm{HF}}^{n}\}$ exists we can write the wavefunction as a linear combination of Hartree-Fock configurations and optimize this linear combination according to the variational principle. This procedure is known as the configuration interaction (CI) method. Thus, finding approximate solutions to the exact Hamiltonian is made tractable by writing the wavefunction as a linear combination of Hartree-Fock configurations. The exact solution is approached in the limit of an infinite basis set (i.e., all possible Hartree-Fock configurations); however, in practice, computational considerations limit us to finite basis sets.

1.3.1.6.2 **Perturbation Theory** The strategy in CI methods is to make use of solutions to the Hartree–Fock equations as the basis set for a linear combination of configurations that can be optimized for the exact, multi-electron hamiltonian within the context of the variational principle. By contrast, perturbation theory rewrites the multi-electron hamiltonian in terms of an analytically solvable component (H_0) and a correction factor (H_1). Møller–Plesset (MP) perturbation theory, takes H_0 to be the sum of the Hartree–Fock one-electron operators, excluding the electron–electron repulsion terms. The perturbation term (H_1) is then taken to be the electron–electron repulsion terms (taking into account the double counting of these interactions in the Hartree–Fock equations). This choice is appropriate insofar as the Schrödinger equation with H_0 is solvable; however, the electron–electron repulsion terms is not always the relatively small perturbation that the theory assumes it to be.

The uncorrected energy from MP includes no electron–electron interactions, and the first-order correction recovers the Hartree–Fock result. Additional correction terms may offer further improvements to the Hartree–Fock energy; however, these terms become increasingly complex and computationally expensive to calculate. Furthermore, the nature of these correction factors means that there is no guarantee that the approximation at any level (beyond the first) provides either an upper or a lower bound to the real energy.

1.3.1.6.3 **Coupled Cluster** Coupled cluster methods provide a way to systematically add various types of excitations to the wavefunction. Thus, the first-order terms include all single-electron excitations, the second-order terms all double excitations, and so on. Coupled cluster methodology resembles the CI approach insofar as it writes the wavefunction as a linear combination of configurations. It resembles perturbation theory in systematically ordering corrections factors from least to most significant.

1.3.1.6.4 **Electron Correlation in Electrochemistry** At present, methods that explicitly include electron correlation are too expensive for use on most systems of interest in electrochemistry. Nevertheless, they occasionally find application calculating dispersion interactions or van der Waals forces, which depend heavily on electron correlations

1.3.1.7 Density Functional Theory

An alternative approach to wavefunction methods, is to work instead with the electron density. Not only is electron density more intuitive, but it also provides computational advantages, which have enabled density functional theory (DFT) to develop into a powerful and widely used methodology.

1.3.1.7.1 **The Hohenberg–Kohn Theorems** Two theorems, first proved by Hohenberg and Kohn [35,36], provide the foundation for DFT. The first of these, the Hohenberg–Kohn existence theorem, states that the non-degenerate, ground-state electron density of a system uniquely determines the external potential of the system (and thus the hamiltonian) within a constant. This means that the system energy can be expressed as a functional of the electron density:

$$E_0 = f[\varrho(\mathbf{r})] \tag{1.23}$$

The second theorem, the Hohenberg–Kohn variational theorem, justifies the application of variational methods to the density. Thus, the correct ground state electron density distribution is the density distribution corresponding to the energy minimum. Thus

$$\frac{\partial f[\varrho(\mathbf{r},\lambda)]}{\partial \lambda} = 0 \tag{1.24}$$

leads to the optimal ground state electron density $\rho_0(\mathbf{r}, \lambda)$.

1.3.1.7.2 **The Energy Functional** Unfortunately $f[\varrho_0(\mathbf{r})]$ is unknown; however, if we consider the electron density to be made up of non-interacting electrons (this is allowed, provided we really have the same density), we can write the energy as a sum of single energy operators:

$$E[\rho(r)] = \sum_{i}^{M} \left(\left\langle \chi_{i} \left| \frac{-\nabla_{i}^{2}}{2} \right| \chi_{i} \right\rangle - \left\langle \chi_{i} \left| \sum_{\nu}^{N} \frac{Z_{\nu}}{|\mathbf{r}_{i} - \mathbf{R}_{\nu}|} \right| \chi_{i} \right\rangle \right) + \sum_{i}^{M} \left\langle \chi_{i} \left| \frac{1}{2} \int_{|\mathbf{r}_{i} - \mathbf{r}'|} d^{3}r' \right| \chi_{i} \right\rangle + E_{\mathrm{XC}}[\rho(r)]$$

$$(1.25)$$

The first three terms correspond to the electronic kinetic energy, the electronnucleus attractions, and the electron–electron repulsions, respectively. The form of these terms is well known; however, the form of the final term, $E_{\rm XC}$ which includes the electron exchange and correlation energies, along with a correction to the kinetic energy term, is unknown. From here, a single-electron hamiltonian is easily extracted:

$$h_{i}^{\text{KS}} = -\frac{\nabla_{i}^{2}}{2} - \sum_{\nu}^{N} \frac{Z_{\nu}}{|\mathbf{r}_{i} - \mathbf{R}_{\nu}|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}_{i} - \mathbf{r}'|} d^{3}\mathbf{r}' + V_{\text{XC}}$$
(1.26)

and

$$V_{\rm XC} = \frac{\partial E_{\rm XC}}{\partial \rho} \tag{1.27}$$

As in the case of the HF method, the energies obtained with this single-electron hamiltonian for each electron in the system can be summed to arrive at the total system energy. However, in contrast to HF, the result is the exact system energy, rather than an approximate energy. The difficulty is that, in contrast to HF, the exact form of $V_{\rm XC}$ is unknown. Thus, utilizing DFT requires approximating this term.

1.3.1.7.3 Exchange–Correlation Functionals A vast number of approximations for $E_{\rm XC}$ have been developed. These (and the DFT methods they are utilized within) can be conveniently classed in rungs on "Jacob's ladder" (Figure 1.3), which span the gap between Hartree results and chemical accuracy [37,38]. On the bottom rung of the ladder are methods which employ the localized density approximation (LDA). Here, the value of $E_{\rm XC}$ at each point is typically borrowed from the value of $E_{\rm XC}$ for a uniform electron gas with the same density as the local density of the point of interest. In any case, the value of $E_{\rm XC}$ depends only on $\rho(r)$.

The next level up is known as the generalized gradient approximation (GGA). Here, E_{XC} depends not only on $\rho(r)$, but also on its gradient, $\nabla \rho(r)$. Including either the Laplacian of the density ($\nabla^2 \rho(r)$), or the local electronic kinetic energies is known as the meta-generalized gradient approximation (MGGA).



Figure 1.3 Jacob's ladder illustrating the hierarchy of approximations used to construct exchange-correlation functionals. Abreviated categorizations of methods are shown to the left of the ladder and the new level of dependence added at each level is shown on

the right. Thus, the exchange-correlation functional at any given rung of the ladder will be a function of not only the quantity or construct directly to its right, but also of all quantities and constructs below it.

The hyper-generalized gradient approximation (hyper-GGA), uses the Kohn–Sham (KS) orbitals to calculate the exact HF exchange. The total $E_{\rm XC}$ is then written as a linear combination of the HF exchange and the $E_{\rm XC}$ from a LDA and/or GGA method.

Finally, at the highest level of "Jacob's ladder" sit generalized random phase methods (RPM). Not only are occupied KS orbitals included, but also virtual (i.e., unoccupied) KS orbitals.

1.3.2

Applications of Electronic Structure to Geometric Properties

The system energy is the most basic output of electronic structure calculations. Due to the Born–Oppenheimer approximation, this calculated system energy corresponds to the energy associated with a particular set of nuclear coordinates (i.e., a particular system geometry). Although the multi-dimensional configuration space containing all possible geometries is often quite large, only a few select geometries, namely local minima and the saddlepoints along the minimum energy pathways (MEP) connecting the local minima, are typically required for an accurate description of the chemical characteristics and behavior of the system. Methods for finding these local minima and saddlepoints, that is, those corresponding to the resting states (RS) and transition states (TS) of a chemical system, are indispensable for successfully applying electronic structure methods to chemical systems.

1.3.2.1 Geometry Optimization

Geometry optimization procedures begin with an initial geometry guess, typically provided by the user based on previous calculations, experimental results or chemical intuition. In addition to the energy of this initial structure, $U(\mathbf{r})$, additional quantities may be calculated in order to aid the following optimization procedure.

The first of these is the energy gradient, $g = -\nabla U(\mathbf{r}) = \sum_{i} -\frac{\partial U(\mathbf{r})}{\partial \mathbf{r}_{i}}$, which corresponds to the net forces exerted on each atom and is expressed as a vector in configuration space, $g = -\sum_{i} F_{i}$. In some cases, the components of the gradient are best evaluated analytically from the function used to compute the system energy, U(r). However, in other cases it is either more efficient or necessary to evaluate them numerically, by displacing the geometry along the various directions in configuration space and computing the energy change that results from each displacement. By definition the gradient at a RS point (or any stationary point including a TS) is zero, thus, the gradient can also be used to help identify the end point of the calculation.

Another useful metric is the second derivative matrix, also known as the Hessian. The matrix components correspond to all possible pairs of coordinates *i* and *j* (including i = j) in configuration space, and have the value: $\left(\frac{\partial^2 U(\mathbf{r})}{\partial \mathbf{r}_i \partial \mathbf{r}_j}\right)$. At a stationary point, all of the off-diagonal terms of the Hessian are zero. In addition, the diagonal terms are all positive at a RS, and all are positive except for one, which is negative, at

a TS. Thus the Hessian can not only be used to verify that a RS has been reached, but can also be used to distinguish between various types of RSs.

The most basic optimization strategy is to optimize the variables (i.e., coordinates in configuration space) one at a time. Because the variables are not independent there is no guarantee that the local minimum will be approached with this procedure, and even should it be approached this is likely to require many optimization cycles. Thus, for systems with more than a handful of variables (i.e., the vast majority of molecular geometries) this method is neither practical nor reliable. Fortunately other strategies are available.

Steepest descent methods optimize the structure at each optimization step along the direction of the gradient of the starting geometry for that step. Convergence is guaranteed using steepest descent methods; however, their efficiency is hampered by their intrinsic requirement that adjacent optimization steps be in perpendicular directions. Conjugate gradient methods attempt to remedy this and improve their efficiency by forming the new search direction from a linear combination of the previous search direction and the gradient of the current geometry.

Newton–Raphson methods take advantage of not only the gradient but also the Hessian to advance the optimization yet more quickly toward the nearest stationary point. Because this stationary point could be a minimum, maximum or saddlepoint, it is important that the initial guess is made within the desired region of configuration space.

1.3.2.2 Transition State Searches

Methods for locating saddle points can conveniently be categorized by the type of input or initial guess that they require. Local methods require nothing more than an initial geometry guess near the transition state [39]. As we have already seen Newton-Raphson methods are available for optimizing an initial input structure to the nearest stationary point (in this case a saddle point). An analysis of which internal coordinates (bond distances, angles, etc.) are significantly different in the products compared with the reactants sometimes provides insight into the region of configuration space in which the saddle point is most likely to be found, suggesting an initial guess. However, this is often not the case, making an acceptable initial guess hard to come by. This difficulty, combined with the high computation cost of calculating the Hessian at each step, makes local methods an impractical sole means for finding most saddle points. At the very least a different preliminary method is needed to arrive at a reasonable initial guess, before turning to local optimization methods. Interpolation methods are able to fill this role. Unlike local optimization methods, they require the minima on either side of the saddle point being sought as inputs [40]. Various schemes can then be used to trace out and optimize a MEP between the given minima. The crest of this MEP then corresponds to the saddle point being sought. In some cases system coordinates can be chosen such that the reaction coordinates are seen to clearly correspond to just one or two of these system coordinates. Constrained minimization, in which these reactive coordinates are stepped from their reactant to their product values, provides an intuitive means of mapping out a reaction pathway, in what is known as coordinate driving. Linearly



Figure 1.4 Illustration of how the NEB method NEB procedure, and the final MEP, at which the would be applied to a two-dimensional potential energy surface to find a transition state. A typical initial guess used to initiate a

application of the NEB method arrives, are shown on the potential energy surface.

interpolating the reactant and product cartesian coordinates is another interpolation strategy, with a variety of strategies for optimizing the interpolated image(s) and driving one of them to the saddle point being available [41]. Particularly popular are variations of the nudged elastic band (NEB) method (Figure 1.4), which uses a spring constant to connect and evenly distribute images over the MEP [42].

1.3.3

Corrections to Potential Energy Surfaces and Reaction Pathways

While local minima and saddle points are the critical locations on a potential energy surface (PES) for describing chemical reactions, there is a collection of system states associated with each of these stationary points on the PES. These associated states include the vibrational, rotational, translational and electronic states of the molecules within the system, as well as configurational states of the system components. Taking into consideration the energetic and entropic contributions of these states is often vital for accurately modeling chemical reactions that might occur in a system.

1.3.3.1 Energy and Entropy Corrections

Vibrational states of molecules are typically treated within a harmonic approximation. In this case, the normal modes, \mathbf{w}_{ν} , and corresponding frequencies, ω_{ν} , are found by solving the eigenvalue equation given by the Hessian:

$$\mathbf{H}\mathbf{w}_{\nu} = \omega_{\nu}^{2}\mathbf{w}_{\nu} \tag{1.28}$$

Once the normal modes are known, the allowed energies and states for each mode are determined by the quantum mechanical treatment of the individual harmonic oscillators. Thus the energy states for a vibrational mode with frequency ω are given by:

$$\varepsilon_n = \hbar \omega \left(n + \frac{1}{2} \right), n = 0, 1, 2, 3, \dots$$
 (1.29)

The total partition function for all vibrational states (n = 0, 1, 2, ...), from which their entropic contributions at temperature T can be extracted, is given by:

$$q_{\rm vib} = \frac{\exp\left[-\frac{\hbar\omega}{2k_{\rm B}T}\right]}{1 - \exp\left[-\frac{\hbar\omega}{k_{\rm B}T}\right]}$$
(1.30)

In cases where gas phase molecules consisting of more than a single atom are present (i.e., where molecules are free to rotate), rotational degrees of freedom should be considered. These are typically accounted for within a rigid rotor approximation, which assumes that the internal geometry of the molecule is fixed. For a diatomic molecule the energy levels obtained from the quantum mechanical solution of a rigid rotor for two masses, m_1 and m_2 , lying distances r_1 and r_2 , respectively, from their combined center of mass, leading to a moment of inertia $I = m_1 r_1^2 + m_2 r_2^2$, are:

$$\varepsilon_{j} = \frac{\hbar^{2}}{2I}j(j+1), j = 0, 1, 2, 3, \dots$$
(1.31)

When we take into account the symmetry index, σ (which is 1 for a heterogeneous and 2 for a homogeneous diatomic molecule), we can write the partition function encompassing all rotational states as:

$$q_{\rm rot} = \frac{2lk_{\rm B}T}{\sigma\hbar^2} \tag{1.32}$$

For more complex molecules with three moments of inertia, I_1 , I_2 and I_3 , the partition function is:

$$q_{\rm rot} = \frac{\sqrt{\pi I_1 I_2 I_3}}{\sigma} \left(\frac{2k_{\rm B}T}{\hbar^2}\right)^{\frac{3}{2}}$$
(1.33)

In the case of gas phase molecules, not only rotational but also translational motion should be considered. The expected energy contribution from translational degrees of freedom for an ideal gas particle with mass *m* at temperature *T* is given by:

$$\langle \varepsilon_{\rm trans} \rangle = \frac{3}{2} k_{\rm B} T \tag{1.34}$$

and the partition function for such a particle constrained in a volume V is:

$$q_{\rm trans} = \left(\frac{mk_{\rm B}T}{2\pi\hbar^2}\right)^{\frac{3}{2}} V \tag{1.35}$$

While there are cases where excited electronic states are low enough in energy to play a significant role, in the majority of cases only the ground electronic state is accessible and thus the ground state energy computed using an electronic structure method provides a good approximation for the electronic energy of the system, E_{elec} . The partition function for this electronic state, q_{elec} is given by its degeneracy, g_0 , that is, its spin multiplicity.

The total system energy can now be computed by summing these various energy contributions:

$$E_{\rm tot} = E_{\rm elec} + E_{\rm vib} + E_{\rm rot} + E_{\rm trans} \tag{1.36}$$

Similarly the overall partition function is formed by taking the product of the various contributing partition functions:

$$Q = q_{\text{elec}} \cdot q_{\text{vib}} \cdot q_{\text{rot}} \cdot q_{\text{trans}}$$
(1.37)

Armed with these energy correction terms and their corresponding partition functions, we are able to calculate a variety of useful thermodynamic quantities, such as the zero-point energy, entropy, enthalpy and Gibbs free energy.

1.3.3.2 Thermodynamic State Functions

A stationary state, and indeed any point on a PES, corresponds to a set of fixed nuclear coordinates. However, the Heisenberg uncertainty principle does not allow for fixed nuclear coordinates, because the positions and momenta of the nuclei would then be simultaneously, exactly determined. Similarly, the absence of a zero-energy state among the vibrational states means that regardless of the temperature (i.e., even as absolute zero is approached), molecules continue to vibrate, albeit only in their lowest vibrational states. Thus meaningful comparison with experiment requires correcting system energies to include these zero-point corrections. Adding these zero-point corrections to the "bottom of the well" energy, E_{elec} , yields the zero-point-corrected energy of the system:

$$E_0 = E_e + \frac{1}{2} \sum_{\omega} \hbar \omega \tag{1.38}$$

This zero-point energy then corresponds to the effective energy in experiments conducted at temperatures approaching 0 K.

Making additional comparisons with macroscopic quantities such as pressure p, temperature T, and volume V requires us to use the tools of statistical mechanics to derive appropriate thermodynamic quantities from the overall partition function, we found above. Thus, the temperature-dependent internal energy of a system at a particular temperature T, U(S, V), can be calculated from its partition function, Q:

$$U(S,V) = k_{\rm B} T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$
(1.39)

An often more relevant quantity is the enthalpy, H(S, p), since it corresponds to experimentally determined heats of formation:

$$H(S, p) = U(S, V) + pV$$
(1.40)

The entropy, S(U, T), of a system can also be calculated directly from the partition function:

$$S(U, V) = k_{\rm B} \ln Q + k_{\rm B} T \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V}$$
(1.41)

Using this entropy both the Helmholtz, A(T, V), and the Gibbs, G(T, p), free energies can also be computed:

$$A(T, V) = U(S, V) - TS$$
 $G(T, p) = H(S, p) - TS$ (1.42)

The Gibbs free energy is particularly useful as it corresponds to the most common experimental conditions (fixed temperature and pressure). Finally, it should be noted that these thermodynamic quantities can not only be computed for individual points on the PES, but that these points can then be used to construct new energy surfaces, corresponding to the thermodynamic quantity of interest.

1.3.3.3 Reaction Energies and Rates

The raw energy from a single electronic structure calculation typically has little meaning on its own for several reasons. First, the use of pseudo-potentials masks the energetic contributions of core electrons. Second, the energy to form the system from infinitely separated electrons and nuclei (or pseudo-potentials when they are used) is almost never directly relevant to experimental measurables. Finally, systematic errors associated with the use of any particular method and basis set tend to result in relatively large errors for a given individual calculation.

If, instead, relative energies are calculated, the situation changes considerably. Approximations and systematic errors often cancel out, yielding much improved accuracy. Furthermore, reaction energies and heats of formation are standard experimentally measured quantities, which are readily available for many reactions and substances.

The heat of formation, $\Delta_f H_{298}^\circ$, of a system composed of *i*-indexed atoms with stoichiometric factors, v_i , and standard state enthalpies, $H_{298}^\circ(i)$, computed from electronic structure calculations as shown above, and an electronic-structure-calculation-derived system enthalpy of H_{2985ys}° is:

$$\Delta_f H_{298}^\circ = H_{298sys}^\circ - \sum_i \nu_i H_{298,i}^\circ$$
(1.43)

Reaction energies, enthalpies and free energies can also be calculated analogously. Thus, the Gibbs free energy for a reaction is given by:

$$\Delta G^{\circ} = G^{\circ}_{\text{products}} - G^{\circ}_{\text{reactants}} \tag{1.44}$$

The Gibbs free energy (or thermodynamic quantity for another relevant ensemble) can then be used to calculate the equilibrium constant for the reaction of interest:

$$K_{\rm eq} = \exp\left[\frac{-\Delta G^{\circ}}{RT}\right] \tag{1.45}$$

This is all the information needed to characterize a system at equilibrium; however, non-equilibrium systems, and in particular reaction rates, are often of interest in electrochemistry. The rate of an elementary reaction step can be written as the product of the concentrations of the reactants, each raised to the power of its

stoichiometric factor, times a rate constant:

$$\text{Rate} = k_{\text{rate}} \prod_{i} [i]^{\mathbf{v}_{i}}$$
(1.46)

Transition state theory provides an approximate means for calculating the rate constant from the initial state (i.e., reactants) and transition state separating the reactants and products on the PES:

$$k_{\text{rate}} = \frac{k_{\text{B}}T}{h} \exp\left[\frac{-\Delta G^{\ddagger}}{RT}\right]$$
(1.47)

where ΔG^{\ddagger} is the free energy difference between the reactants and the transition state. The critical assumption here is that the system begins in the reactant state and then samples nearby states until at last it samples the transition state, at which point it proceeds directly to the product state. Thus, the exponential term can be interpreted as the Boltzmann factor for finding the system at the transition state, and the forefactor gives the rate at which new states are sampled.

1.3.4 Electronic Structure Models in Electrochemistry

Traditional electrochemical experiments involve systems composed of around 10^{26} atoms. However, with current computational technology, routine electronic structure calculations are only feasible for around 10^2 atoms. Thus, modeling macroscopic-scale experimental systems with nano-scale electronic structure calculations requires the three following assumptions or approximations. First, the assumption that the experimental system can be broken up into various spatially localized processes (e.g., electrochemical reactions at the interface or ion diffusion in the electrolyte). Secondly, that the macroscopic properties of these processes can not merely be derived from the sum of all underlying atomistic processes, but rather, that they can be derived from the properties of a limited number of representative exemplars of the atomistic processes (rather than summing them exhaustively). Finally, that there are models involving no more than 10^2 atoms which reliably represent the critical atomistic processes in the macroscopic system and can thus be used as the exemplars that form the starting point for derivations of macroscopic properties.

The most commonly modeled processes and regions using electronic structure calculations are the chemical reactions at the interface between the ion- and electronconductors. Typically, this is a solid–liquid interface. The number of atoms explicitly involved in an individual electrochemical reaction at such an interface is typically within the limits of the number of atoms that can be explicitly treated with electronic structure methods. The electrode surface, as well as the surrounding electrolyte, often plays a crucial role in surface reactions; however, both extend well beyond the nano-scale limitations of electronic structure calculations into the macroscopic scale. Thus, the application of electronic structure methods to electrochemical surface reactions, requires restricting the extent to which the solvent and surface are treated explicitly (i.e., modeled as individual atoms).



Figure 1.5 Illustrations of slab (a) and cluster (b) methods for modeling an electrode surface. In the slab approximation, the electrode surface is modeled using a periodically infinite slab. This infinite slab (with a periodically recurring adsorbate) is shown below, while the contents of a single simulation supercell are shown

above among the outlines of neighboring supercells. In the cluster approximation a cluster is conceptually lifted out of the electrode surface, and taken to be representative of the whole on the basis of convergence tests, where various cluster sizes and geometries are tested.

1.3.4.1 Modeling the Electrode Surface: Cluster versus Slab

There are two basic approaches for modeling extended electrode surfaces: the cluster approach and the slab/supercell approach (Figure 1.5) [27,43-45]. In the cluster approach a cluster of atoms surrounding the active surface site, where the reaction is to take place, is cut out and used to model the electrode surface. In determining which particular cluster model to use, tests should be performed to verify that the cluster chosen well approximates the chemical activity of the active site for the reaction of interest. Because computational capabilities were once much more limited than they are today, clusters were a popular model choice, because a cluster can be formed with as few as a single atom. However, many of these early, small cluster models have been found to result in inadequate, if not altogether false, descriptions of the surface chemistry. Indeed, it has been shown that clusters consisting of 20 to more than 50 atoms are required to reliably model the simplest metal surfaces [46]. Thus it is important to verify that one's results are converged with respect to cluster size before adopting a cluster model. Cluster models are particularly appropriate for studying isolated reactions, in which no neighboring adsorbates are involved. In contrast to cluster models, which limit the extent of the

electrode in all directions, slab/supercell methods limit only the depth of the electrode. Infinite extent in the directions perpendicular to the surface is procured by introducing periodicity. Convergence should be tested to verify that the slab is sufficiently thick to model the surface of a bulk system. The convergence for unit cell lengths perpendicular to the surface is also important to verify when low surface coverage situations are being modeled. Otherwise these unit cell lengths can be modified to correspond to the surface coverage being modeled.

1.3.4.2 Modeling the Solvent: Explicit versus Implicit

The simplest way to deal with the electrolyte or surrounding solvent molecules in electronic structure calculations is to assume that they do not exist. Such gas phase models are appropriate for modeling many surface science experiments, especially under ultra high vacuum (UHV) conditions, however; solvent effects often exert significant influence on surface chemistry in electrochemical environments. Two strategies are used to include these important solvent effects in electronic structure calculations. They are known as explicit and implicit solvation methods (Figure 1.6). In explicit solvation methods a limited number of explicit solvent molecules directly surrounding the solvated molecule model solvation. This procedure is particularly important when one of these solvent molecules plays a chemical role in the reaction, such as temporarily donating a proton. Nevertheless, explicit solvation is not only computationally expensive, but cumbersome. Each additional explicit solvent molecule not only increases the number of electrons in the system, but increases the number of possible solvent configurations that must be tested in order to find the optimal solvent configuration. Furthermore, because DFT does not well describe the van der Waals forces, which are often important in solvation interactions, there is no guarantee that even a large number of optimally placed solvent molecules in a DFT calculation will adequately describe solvation effects.

(a) **Explicit solvation model**



Figure 1.6 Illustrations of explicit (a) and implicit (b) treatments of solvation. In an explicit solvent model, the solvent is modeled using a limited number of explicit solvent

(b) Implicit solvation model



molecules. In an implicit solvent model, the effects of the solvent are typically included in the form of an electric field surrounding the solute molecule(s).

To avoid the computational expense of explicit solvation methods, implicit methods have been developed. These methods assume that solvation effects primarily result from electrostatic interactions, and that the effect of the solvent on the solvated molecule can thus be reasonably represented as an electric field, known as the reaction field. To do this the solvent is modeled as a continuous dielectric with a cavity in the region of the solvated molecule. The polarization of the solvent can then be solved for based on the charge distribution of the solute in the cavity, yielding an electric field in the cavity which acts on the solvated molecule. A self-consistent solution can be approached by solving for the solvent polarization and then its subsequent effect on the solvated molecule as a part of each SCF iteration.

1.3.4.3 Modeling the Electrode Potential

The electrode potential is a critical element in an electrochemical system and distinguishes electrochemistry from simple catalysis. The electrode potential affects electrochemical reactions in two ways. First, because it relates to the chemical potential difference of electrons at the anode and cathode, it determines the energy for transferring an electron between electrodes following each oxidative process at the anode and each reductive process at the cathode. Thus, the electrode potential determines the chemical potential of electrons involved in electrochemical half-cell reactions. Electronic structure calculations typically consider neutral systems and thus do not include the electron transfer between electrodes. However, this can be included in the free energy of the half-cell reaction by including an additional potential-dependent term. Thus the free energy of a reaction that produces z electrons at an electrode at potential U is:

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} - zeU \tag{1.48}$$

where e is the charge of an electron.

Secondly, the electrode potential attracts oppositely charged counter ions, which form a double layer region above the surface, across which an electric field is induced. This electric field influences the structures and energies of surface adsorbates and reactions.

There are three general approaches for handling this induced electric field. The first is to ignore it altogether and treat the electrode potential as solely affecting the chemical potential of electrons (i.e., the fermi level of the system). The second approach is to include an applied external field in the calculations. This is typically carried out within the supercell approach by introducing a dipole layer into the vacuum region between slabs. The primary difficulty here is knowing how strong the electric field, **E**, induced by the electrode potential, *U*, is [47]. If the double layer thickness, *d*, can be estimated [48], then this can be approximated (assuming a plate-capacitor) as:

$$|\mathbf{E}| = \frac{U}{d} \tag{1.49}$$

The third approach is to place a net charge on the electrode. In the case of a slab model (i.e., periodic boundary conditions) counter charges are required to keep the cell neutral. They can be introduced in the form of a uniform background charge, a localized counter

electrode or explicit counter ions. Some care should be taken in doing this, as artifacts are known to arise, particularly in the case of a uniform background charge.

Once the slab is allowed to take on a net charge, it is not only possible to set this charge explicitly by fixing the number of electrons, $N_{\rm e}$, but also implicitly by fixing the chemical potential of the electrons associated with the slab, $\mu_{\rm e}$. While the latter approach more directly models a fixed electrode potential, calculations with a fixed number of electrons are typically sufficiently faster that it is more efficient to vary $N_{\rm e}$ over several calculations until the value corresponding to the desired $\mu_{\rm e}$ is found, than to restrain $\mu_{\rm e}$ directly within the electronic structure calculations.

1.3.5

Summary

This section began by reviewing some of the fundamental principles of quantum mechanics. Central to the application of these principles is the Schrödinger equation, which is typically too complicated to allow for exact solution. A series of approximations was then outlined, which led to a range of methods for calculating approximate electronic wavefunctions (or electron densities in the case of DFT) and electronic energies. The first of these approximations was the Born-Oppenheimer approximation which, by separating the nuclear and electronic components of the wavefunction, leads to a potential energy surface defined by the electronic energy corresponding to each set of possible nuclear coordinate values. Optimization procedures can then be used to locate local minima and saddle points on this potential energy surface, which correspond to stable molecular geometries and transition states, respectively. Vibrational modes can be derived from further analysis of these stationary points, which can then be used to derive a variety of thermodynamic quantities for the chemical species represented by stationary points on the potential energy surface. Finally, the application of transition state theory allows derivation of kinetic reaction rates from these thermodynamic quantities. Thus, electronic structure methods can be used to provide both thermodynamic and kinetic properties of chemical species and reactions to which they are applied.

Electronic structure methods are most commonly used in electrochemistry to model chemical reactions on electrode surfaces. In addition to the atoms directly involved in the reaction of interest there are three system components which need to be considered in developing a reliable model: the electrode surface, the solvating electrolyte, and the electrode potential. The electrode surface is modeled using either a finite cluster or an infinite slab. In either case it is crucial to verify that the cluster or slab used is sufficiently large and well-formed to reliably model the catalytic properties of a macroscopic electrode. Depending on its anticipated role in the reaction, the electrolyte solvent can be modeled either implicitly, using an applied electric field to simulate its electrostatic influence on the system, or explicitly by including a small number of solvent molecules in the calculation. Finally, the influence of the electrode potential can be accounted for by adjusting the fermi level of calculations after their completion. Additionally, it is possible to include the effects of the electrode potential in forming a double layer, either by applying an appropriate external electric field to the calculation directly, or by placing a net charge on the electrode, which induces a similar effect.

1.4 Molecular Simulations

The equations of quantum mechanics are complex and computationally expensive to solve, even in approximate forms. This drastically limits both the size of the systems which it is feasible to treat quantum mechanically, as well as the number of energy calculations that can be performed on a given system. Force field methods use classical-like forces to approximate the quantum mechanical interactions between atoms and molecules in order to decrease the computational expense of calculating these forces by many orders of magnitude. Thus, at the molecular level, intuitive concepts of chemical bonding are used to embed quantum mechanical effects and phenomena into a classical framework.

The aim of this section is twofold: first, to briefly describe the conceptual foundations and practical development of force fields typically used in molecular simulations; second, to consider various ways in which force fields can be applied to electrochemical systems in terms of both simulation techniques and model systems. Strategies for realizing both sequential and concurrent coupling with the electronic structure methods presented in the previous section are also discussed. More complete treatments of molecular simulation methods [25,26,49,50] and additional details relating to particular methods or applications are available in the references cited in the chapter, as well as in many others.

1.4.1

Energy Terms and Force Field Parameters

A force field is a set of equations for calculating the potential energy of a system of atoms. The system energy is computed by summing energy contributions derived from various types of interatomic interactions, as shown in Eq. (1.50).

$$V_{\rm sys} = V_{\rm bond} + V_{\rm angle} + V_{\rm torsion} + V_{\rm coulomb} + V_{\rm vdW} + \dots$$
(1.50)

These potential energy contributions are typically calculated as functions of the system geometry. Parameters in the energy expressions are typically fit to experimental or computational data. In spite of the wide variety of functional forms used by various force fields to compute the individual energy terms, the widespread agreement among them regarding the types of energy contributions that need to be included reveals an underlying conceptual unity.

1.4.1.1 Covalent Bond Interactions

Energy terms in most force fields can be divided into two classes: those associated with covalently bonded atoms (i.e., with covalent bond dependence) (Figure 1.7) and those associated with all pairs of atoms (i.e., no covalent bond dependence).



Figure 1.7 Schematic representation of covalent bond interactions. The bond energy is primarily a function of the internuclear bond distance, r_{ij} , between atoms *i* and *j*.

1.4.1.1.1 **Reactive versus Non-Reactive** Whether a force field is "reactive" or not (i.e., describes changes in chemical bonding) is the most fundamental distinction between force field types. Reactive force fields compute a covalent bond order as a function of interatomic distances, and allow it to continuously vary between zero and full bond order (1, 2 or 3 depending on the atoms involved), such that a physically reasonable description of bond formation and cleavage is given [51–53]. Furthermore, other bond-dependent quantities scale with this continuous bond order as it varies between zero and full bond order. Because chemical reactions may result in an atom converting from one type or configuration to another (e.g., one orbital hybridization or oxidation state to another), a universal description of each atom within the force field must adequately model all of these possible forms.

In the case of non-reactive force fields whole number covalent bond orders are predetermined in the input or computed from initial bond distances. These covalent bond assignments are then maintained for the duration of the simulation. Thus, different atom types (i.e., force field descriptions) can be used to describe the same element in different chemical bonding configurations.

1.4.1.1.2 **Covalent Bond Strength** The most basic function of covalent bond energy terms is to describe the energy associated with stretching or compressing the bond. For the small changes associated with molecular vibrations, a harmonic oscillator provides a simple model of the energy associated with stretching or compressing the bond (Figure 1.8). Thus, the simplest non-reactive force fields calculate the energy associated with stretching or compressing a harmonic oscillator, in which case the bonding can be described by Eq. (1.51):

$$V_{\text{bond-harmonic}} = \sum_{i,j \neq i} \frac{1}{2} k_b \left(r_{ij} - r_0 \right)^2.$$
(1.51)

This equation is known as Hooke's law, where r_0 denotes the equilibrium distance and k_b the force constant of the bond. The total bond potential is the sum over all bonds.

Describing covalent bond energies using harmonic oscillators forbids dissociation, because the energy increases quadratically as the bond is stretched, whereas dissociation requires the covalent energy function to level off at the dissociation energy within a couple of angstroms of the equilibrium bond distance. Nevertheless, further excessive bond compression should result in high energies due to nuclear– nuclear repulsions. Thus, a function describing the covalent bond energy must be asymmetric, with one side of a harmonic-like well climbing steeply to represent



Figure 1.8 Graphic representation of common expressions used to compute covalent bond energies or energy deviations. A harmonic potential can be used to compute the energy for reactive force field. \vec{r}_{ii} between two atoms i and displacing covalently bonded atoms from their

equilibrium distance within a non-reactive context. A Morse potential can be used to describe covalent bond formation/cleavage in a j, and the force constant k_b .

internuclear repulsions, while the other side of the well gradually flattens out as the atoms dissociate. The Morse potential is a simple function meeting these criteria, and is one of the simplest choices for a reactive internuclear covalent energy expression (Figure 1.8). It can be written in terms of a minimum interatomic potential energy, $D_{\rm e}$, a corresponding equilibrium distance, r_0 , and a factor, α , related to the well stiffness and hence the allowed vibrational modes.

$$V_{\text{bond}-\text{Morse}} = \sum_{i,j \neq i} D_{\text{e}} (1 - \exp[-\alpha(\vec{r}_{ij} - r_0)])^2$$
(1.52)

In both reactive and non-reactive force fields it is convenient to reference the energy at the bottom of the covalent bond well to the bond energy relative to some standard state of the atoms. This means that the computed energies have some intrinsic, independent meaning, and not simply relative values for comparison with other structures one explicitly calculates. A further requirement for reactive force fields is that the depth of the covalent bond energy function (i.e., the energy at the bottom of the well compared with the energy at the dissociation limit) must correspond to the bond energy relative to the dissociated atoms.

1.4.1.1.3 Angles Describing geometries of molecules involving more than two atoms involves not just bond distances, but also bond angles involving three bonded atoms (two atoms each bonded to a third, central atom). Angle energy terms are typically computed as penalties based on the difference between the actual value of the angle and its optimal equilibrium value. Thus they correct the energy for deviations from the optimum geometry. Equation (1.53) shows how energy contributions related to angles might be computed within a harmonic



Figure 1.9 Schematic representation of the angle contribution. This contribution is described by the force constant k_{Θ} and the angle Θ_{ijk} .

approximation for displacements from an equilibrium angle.

$$V_{\text{angle}} = \sum_{i,j,k} \frac{1}{2} k_{\Theta} \left(\Theta_{ijk} - \Theta_0\right)^2$$
(1.53)

 k_{Θ} denotes the force constant, Θ_{ijk} the angle between the bonds as shown in Figure 1.9 and Θ_0 the equilibrium angle.

1.4.1.1.4 **Torsion** The energy associated with rotation about a chemical bond is given by a torsional energy term which, like angle terms, is computed as an energy penalty for deviations from an optimal, equilibrium dihedral angle θ_0 (Figure 1.10). Unlike angle terms, where only small deviations from equilibrium are expected, torsional angle terms need to be able to account for all possible dihedral angles, since full rotation is common. Thus a periodic function is needed. The following abbreviated Fourier series provides a simple expression for the torsional energy:

$$V_{\text{torsion}} = \sum_{\text{Quadrupletts}} \sum_{n=0}^{3} \frac{1}{2} V_n [1 + \cos(n\phi - \delta)]$$
(1.54)

Which terms in the *n* summation are non-zero will depend on the geometry of the rotation. For example, rotation about the double bond in ethene has a periodicity of 180° and so only the n = 2 term is non-zero. Analogously, rotation about the single bond of ethane has a periodicity of 120° , so that only the n = 3 term is needed. If one of the hydrogen atoms on each carbon is replaced with another substituent, then the n = 1 term is needed to differentiate between the various minima. Additional



Figure 1.10 Schematic representation of the torsional deformation. This deformation is described by the angle of intersection between the two planes, which are defined by the atoms *i*, *j*, *k* and *j*, *k*, *l*, and the force constant V_n .



Figure 1.11 Schematic representation of out-of-plane energy correction for central atom *k* with respect to the plane defined by atoms *i*, *j* and *l*.

combinations and/or higher order terms may be used to model more complex situations.

In the case of reactive force fields it is important for these correction terms to vanish as any one of the covalent bonds involved in the torsion or angle dissociates. Otherwise the penalty will be falsely imposed on groups of non-bonded atoms. Polynomial expressions are typically used to model angle displacements, and trigonometric functions are most often used for torsions.

1.4.1.1.5 **Inversion** An sp² atom with three planar substituents should suffer relatively large energetic losses for displacement from the plane its substituents occupy. Because the angle correction terms are not strong enough to account for these forces, an additional inversion energy term is often included for such atoms. The simplest way to express the inversion energy is as a harmonic function for displacements measured in terms of the distance, *d* of the central atom from the plane defined by its substituents and an empirically chosen spring constant, α . See Figure 1.11.

$$V_{\text{inversion}} = \sum_{k} \frac{1}{2} \alpha d^2 \tag{1.55}$$

1.4.1.1.6 **Under/Over Coordination** In reactive force fields penalties for under- and over-coordination (i.e., an atom forming too many or too few covalent bonds) are sometimes used to enforce proper covalency. To do this the total bond order associated with an atom is computed by summing the bond orders of the covalent bonds the atom is involved in. Then an energy penalty is assigned depending on how much this total bond order falls below or surpasses the expected, optimal total bond orders by correcting the bond orders so that bond orders involving atoms whose valencies are not fully filled (based on preliminary bond orders) are enhanced, while bond orders involving over-coordinated atoms are diminished.

1.4.1.1.7 **Cross Terms** Additional terms can also be introduced to correct for the interactions between the various terms. For example, the equilibrium C-H bond distance in methane, should be dependent on the H-C-H angles. The

introduction of such cross terms can be useful in reducing the number of different atom types required to adequately represent a given element.

1.4.1.1.8 **Resonance** An extra energy term is required to stabilize resonant structures in conjugated systems. This energy can be added into non-reactive force field descriptions, either by developing an additional atom type to correspond to each bonding combination that results in resonance or by adding correction values from crude electronic structure calculations. For reactive force fields this terms comes into play when successive bonds have bond orders near 1.5.

1.4.1.2 Non-Covalent Interactions

Beside interactions associated with covalent bonds, several interactions between atoms which are not associated with covalent bonds are important. These interactions can be defined as occurring only between non-bonded pairs of atoms. Alternatively, when the strengths of the covalent bond interactions are adjusted to compensate for their presence, they can be evaluated for every pair of atoms.

1.4.1.2.1 **Electrostatics** Electrostatic interactions are typically modeled by approximating individual atoms with point charges *q*, whose energy of interaction is given by:

$$V_{\text{coulomb}} = \sum_{i} \sum_{j < i} \frac{1}{4\pi\varepsilon_{ij}} \frac{q_i q_j}{r_{ij}}$$
(1.56)

The partial charges associated with the atoms are either assigned based on the results of experiments or theoretical measurements, or are computed within the force field based on the system geometry and relative electronegativities of the atoms. The permittivity (ε_{ij}) is often assigned empirically to match experimental data or higher level calculations rather than being derived from first principles. See Figure 1.12.



Figure 1.12 Schematic representation of electrostatic interactions between atoms *i* and *j*, carrying partial charges q_i and q_j , respectively. The interaction energy is then calculated based on these partial charges, the distance between *i* and *j*, r_{ij} , and the permittivity of the medium, ε_{ij} .



Figure 1.13 Schematic representation of the Van der Waals contribution. This contribution is described by a Lennard-Jones potential.

1.4.1.2.2 **Van der Waals** A second important class of non-bond interactions are van der Waals interactions. These forces result from temporarily induced dipoles, as two atoms approach another (Figure 1.13). A variety of potential energy expressions can be used to describe van der Waals interactions. The Lennard-Jones potential (also known as a 12-6 potential, where the numbers refer to the repulsive and attractive exponents which make up the potential) is the one most frequently used (Figure 1.14). It is given in Eq. (1.57):



Figure 1.14 Graphical representation of the Lennard-Jones potential, showing its attractive and repulsive components.

Thus, van der Waals forces are attractive at large values, but repulsive for small values of the internuclear separation r_{ii} .

1.4.1.2.3 **Hydrogen Bonds** Hydrogen bonding is often partially accounted for in the van der Waals, and electrostatic terms; however, an additional correction factor is useful for improving the description of hydrogen bonds. This attractive interaction between hydrogen H_i and an atom X_j to which it is hydrogen bonded, is often modeled as:

$$V_{\text{Hbond}} = \sum_{i} \sum_{j} V_0 \left[5 \left(\frac{r_0}{r_{\text{ij}}} \right)^{12} - 6 \left(\frac{r_0}{r_{\text{ij}}} \right)^{10} \right]$$
(1.58)

This closely resembles the Lennard–Jones potential used to model van der Waals forces, except that the attractive region disappears more quickly as the interatomic distance increases.

1.4.2

Parametrization and Validation

The many equations that make up a force field involve a number of parameters. These parameters must be obtained somehow. One possibility is fitting them to experimental data; however, the amount of relevant experimental data available for fitting force field parameters is often miniscule compared with the number of parameters that need to be established. Thus, a second alternative is to use data from electronic structure calculations to find suitable force field parameters. This second approach is a classic example of serial multiscale modeling. Results obtained from electronic structure methods provide the input for a molecular model.

Parameters are typically fit by minimizing some measure of the error they result in when results they produce are compared with the training set data. This can be accomplished by either fitting individual parameters to particularly relevant parts of the training set, or by fitting groups of parameters to larger subsets of the training set. A variety of mathematical tools and computational algorithms is available for optimizing force field parameters, however, it is important to keep the physical nature of the parameters in mind (i.e., magnitude and qualitative behavior of the energies they produce), so that the various energy terms continue to correspond to the chemical concepts they were designed to represent. The physical reasonableness of a force field formulation thus provides an important justification for applying the force field to systems which are not explicitly included in the training set. Nevertheless, it is important to know the limitations of an individual force field and to use caution when applying it to a system in which the atomic interactions deviate significantly from those contained in the training set.

A given parametrization can be validated using one of three different types of tests. The first type of test uses the parameters to reproduce data that were not included in the training set, but which are of the same type (e.g., energies of formation from DFT) as that contained in the training set. If the parameters are able

to reproduce this data, it suggests that their validity extends beyond the immediate confines of the data they were trained against. A second way of using QM results to validate a parametrization is to extract novel structures or reaction pathways, which are observed during the course of simulations making use of the parameters, and verify that QM calculations indeed predict similar structures and energies for these snapshots. Returning to a previous level of modeling in order to verify the reliability of the newly established level is an important, although often overlooked, step in building a robust, multiscale framework.

The third type of test involves reproducing larger scale macroscopic properties, which are known experimentally, but cannot be directly reproduced using the electronic structure methods used to produce all or most of the training set (e. g., the melting point of a solid). This final validation procedure is useful in verifying that the parameters describe not only the atomistic phenomena predicted by electronic structure methods, but also higher order experimentally observable phenomena they are designed to model on the basis of the atomistic interactions.

1.4.3 Atomistic Simulations

While the behavior of some systems can be accurately characterized by exploring only the few points in phase space which correspond to selected local minima and the saddle-points connecting them, broader regions of phase space must be explored to reliably model other systems. Small molecules under UHV provide a good example of the former type because the vast majority of intermolecular interactions involve only a pair of molecules. Liquids provide a typical example of the latter type, because the relatively weak, but nevertheless significant interactions between molecules support a vast number of molecular configurations with similar energies.

The relevant local energy minima and transition states between these are too numerous to make an explicit, systematic search a practical computational tool. Furthermore, average thermodynamic properties of such systems, rather than detailed snapshots, are typically what we want to extract from the simulations. A representative sample of configuration space is sufficient for this task. Atomistic simulation techniques provide us with strategies for obtaining such representative samples.

Because a large number of structures must be sampled to provide a representative sampling of a region of phase space, less computationally intensive methods are generally preferred for computing the necessary system properties for each sampled configuration. Thus atomistic force fields provide the most common PES description used in atomistic simulations. Nevertheless, methods, such as Car–Parrinello (CPMD) [54], Born–Oppenheimer (BOMD) [55] and Ehrenfest molecular dynamics [56] have been developed to utilize electronic structure methods in molecular simulations.

1.4.3.1 Monte Carlo Methods

Monte Carlo (MC) methods [49,57] provide a means of randomly exploring phase space starting in the region of an initial structure. For each simulation

step a random number determines how to perturb the system. The energy of the perturbed system is then calculated and compared with the energy of the system prior to the perturbation. If the energy of the system has decreased, then the new structure is automatically accepted. If the energy of the system increases by ΔE then the Boltzmann factor $e^{\frac{-\Delta E}{B_B I}}$ is compared with a random number between 0 and 1. If the Boltzmann factor is larger than this random number, then the new structure is accepted. This enables a thermodynamically weighted sampling of configuration space at the chosen temperature, *T*, while still allowing for the possibility of overcoming energy barriers to sample configuration space beyond the valley in which the structure of the initial guess lies.

One of the advantages of MC methods is that nearly any conceivable internal or external system coordinate can be used as the variable to be perturbed in generating new structures. Cartesian coordinates, bond distances and angles can be perturbed, atom positions can be exchanged, or atoms can even be added to or removed from the system.

1.4.3.2 Molecular Dynamics

The ergodic hypothesis implies that, regardless of the initial state we choose, if a thermodynamic variable is monitored as we follow the dynamical trajectory of the system, its value will converge to the appropriate statistical, expectation value as the time approaches infinity. In practice this means that, if followed over a sufficiently long time period, the system dynamics provide a thermodynamically representative sampling of a system. Typically this is accomplished by applying Newton's second law to determine the motion of the atoms.

$$m\frac{\partial^2 \mathbf{r}}{\partial t^2} = -\nabla V \tag{1.59}$$

Here, *V* represents the potential energy surface, which can be mapped out piece-wise using a force field, electronic structure or other method for computing system energies. For all but the most trivial systems, analytical solutions to these equations are not readily available. Thus the dynamics are propagated by using a variety of numerical algorithms (e.g., Verlet, leap-frog or velocity Verlet [58]) to estimate the particle positions and velocities across finite time intervals. The smaller these time intervals or time steps, the better simulation approximates the true trajectory; however, smaller time steps mean that more simulation time is required to explore phase space. Meaningful trajectories typically require time steps which are at least an order of magnitude shorter than the fastest process in the system. Typically these are vibrational frequencies with an order of magnitude of 10^{14} s⁻¹, so that time steps of the order of 10^{-15} are necessary.

Because the application of Newton's second law of motion (Eq. (1.59)) conserves energy, the natural ensemble for molecular dynamics (MD) simulations is the NVE ensemble, in which the number of each type of particle (N), the system volume (V) and the energy of system (E) are held constant. However, algorithms for simulating other ensembles, in which the chemical potential (μ) might be held constant instead of N, or the external pressure (P) instead of the system volume, or the system temperature (T) instead of E, have also been developed (e.g., NVT, NPT, μ VT) [59].
1.4.3.3 QM/MM

While force field parameters are often arrived at by means of a serial approach to multiscale modeling, it is also possible to combine molecular and electronic structure approaches to coherently model a single system using a concurrent approach to multiscale modeling, known as QM/MM modeling [60]. This approach is suited for systems in which properties better described by electronic structure methods (e.g., reactivity, electron density) are important in only a small portion of a large system. This smaller subsystem is modeled using an electronic structure method (i.e., using the principles of quantum mechanics, QM), while the rest of the system is described by an atomistic force field (i.e., using molecular modeling, MM). The system energy is then the sum of the energies of the isolated QM and MM regions in addition to their interaction energy (see Figure 1.15).

The way in which a system is divided into QM and MM regions and the manner in which these two regions are subsequently coupled are the defining characteristics for any QM/MM method. Location (as determined either by cartesian coordinates or chemical connectivity) often plays a decisive role in assigning atoms and molecules to either the QM or MM region, such that only atoms located in the vicinity of the reaction (or other phenomenon of interest) are treated with QM. This region can be either fixed or allowed to vary throughout the simulation as the reaction spreads or migrates. The assignment of atoms to either the QM or MM region can either take place once for all at the beginning of the simulation, or the atoms can be reassigned at regular intervals based on their up-to-date locations.



Figure 1.15 Schematic representation of a QM/MM simulation. The QM-region is defined by balls and sticks, the MM-region in licorice. The QM/MM boundary region is represented by a blue net surrounding the QM region.

Methods for coupling the QM and MM regions can be divided into two basic categories: mechanical embedding (ME) schemes and electrostatic embedding (EE) schemes. These two general approaches differ in the degree and manner of electrostatic coupling between the two regions. In ME schemes, the QM region is first treated without reference to the surrounding MM region. The electronic structure results for the QM system are then reinterpreted into MM terms and, as such, embedded into the molecular description of the MM region. Thus, perturbations in the electronic structure of the QM region from electrostatic interactions with the MM region are ignored. A second potential problem with ME is that it is often difficult to find an appropriate MM description of the QM region, as the lack of such a description was likely one of the motivations for turning to a QM/MM approach. The primary advantage of the ME approach is its relative simplicity.

Instead of being ignored (as is the case in ME approaches) EE schemes include the electrostatic influence of the MM region on the QM region by introducing point charges, and possibly higher order multipoles (indeed, finding a way to do this efficiently and accurately is a key challenge in the implementations of EE schemes), into the electronic structure calculations, representing the electrostatic influence of the MM region. Thus, polarization of the electronic structure of the QM region by the electrostatic influence of the MM region is enabled. In turn the QM region should be allowed to polarize the MM – and, indeed, there are self-consistent methods available for reaching electrostatic equilibrium – however, this effect is typically ignored. Nevertheless, EE schemes are able to avoid the key disadvantages of ME schemes; however, the simplicity and computational efficiency of the ME approach is lost.

Depending on the system geometry, it may be necessary to draw the QM–MM boundary such that it separates covalently bonded atoms. This is problematic for the atom left in the QM region, because it is left with dangling bonds, which need to be incorporated into covalent bonds for a reliable description of its electronic structure. This is typically accomplished by adding either link atoms or so-called "localized orbitals" to rebuild covalent bonds severed by the QM–MM boundary. The link atom approach typically replaces the missing atom in a severed covalent bond with a hydrogen atom, which is positioned to recreate, as best as possible, the original covalent bond. This approach is popular because it is fairly straightforward and easy to generalize. When an EE scheme is used, care must be taken to ensure that nearby point charges (representing the missing atoms from the severed covalent bonds) do not induce artificial polarization of the covalent bond.

Localized orbital approaches, on the other hand, are more fundamental, but also more complicated to implement. In one version, strictly localized bond orbitals (SLBOs) are determined from calculations of analogous bonds in small molecules. The SLBOs are then included in the electronic structure calculations, but not allowed to mix with any other orbitals during SCF optimization. Yet another option is to replace the missing atoms with complete sets of s + 3p orbitals. Their hybridization (sp^3 , sp^2+p_z , etc.) is determined by the local geometry/coordination and only active orbitals (i.e., those involved in the severed covalent bond) are included in SCF optimization. The key disadvantage with these localized orbital approaches is that a new localized orbital must be developed to accurately describe each unique covalent bond.

1.4.4 Sampling and Analysis

Abstracting reliable information from molecular simulations depends on having a representative sample with respect to the properties or behaviors of interest. This typically requires equilibrating the system by performing dynamics until any biases in the initial configuration of the system have been randomized away. Following the equilibration period, measurements can be made on the further dynamics of the system. This further portion of the simulation must be extensive enough for the relevant regions of phase space to be adequately explored for satisfactory representation in the property extracted. Performing multiple simulations with independent initial configurations provides an alternative strategy for obtaining a statistically meaningful sampling of configuration space.

A vast assortment of information, ranging from macroscopic thermodynamic properties to average structural properties to individual atomistic steps in reaction mechanisms, can be extracted from appropriate molecular simulations. Thermodynamic properties, such as temperature and pressure, are easily calculated from the atomic positions and momenta using their statistical mechanical definitions. Structural motifs can be extracted by calculating radial distribution functions for various atom types in the system, or assigning molecular bonding based on interatomic distances. Entropy and related properties can be extracted from the auto-correlation function [61-64].

1.4.5

Applications of Molecular Modeling in Electrochemistry

Molecular methods have not enjoyed the same level of popularity for applications in electrochemistry enjoyed by electronic structure methods. A large part of this is probably due to the inability of the vast majority of force fields to describe the reactive events which are at the heart of electrochemistry. Nevertheless, several non-reactive aspects of electrochemical systems have been modeled extensively using molecular force fields. The structure of metal-electrolyte interfaces has been one popular subject for such studies [50]. Another has been the solvation of ions in the electrolyte solution and their adsorption on the electrode surface [50]. The structure and stability of the electrochemical double layer that forms above the electrode surface has been a third [65]. In all of these cases statistical averaging over molecular dynamic trajectories is typically used to arrive at a description of the interfacial structure.

The recent advent of force fields capable of describing chemical reactions opens the door to studying catalytic events, similar to those currently investigated using electronic structure methods, only over a significantly larger time and length scale. This has indeed already been realized to a limited extent [66]; however, there are many more systems to which this approach might yet be fruitfully applied.

1.4.6 Summary

This section began with an overview of various energy terms which can contribute to force field descriptions of molecular systems. The use of results from electronic structure calculations to optimize force field parameters in the process of force field development is a quintessential example of serial coupling. Monte Carlo and molecular dynamic simulations are two strategies for sampling the potential energy surface defined by a force field in order to extract information about the chemical system it describes. It is also possible to use molecular force field and electronic structure methods to simultaneously describe different regions of the same system in what are known as QM/MM methods. These are a classical example of a concurrent coupling approach to multiscale modeling. Molecular modeling techniques have been applied to aspects of electrochemistry, especially the electrochemical double layer and other electrode–electrolyte interfaces. The ability to employ reactive force fields to study electrochemical reactions traditionally confined to electronic structure methods has recently opened up exciting opportunities in this arena.

1.5 Reaction Modeling

1.5.1 Introduction

The system descriptions used for the molecular level simulations described in the previous section were primarily physical, rather than chemical. Chemical properties, such as covalency, are indeed typically included in force fields; however, they are included under a physical, as opposed to a chemical, guise. In other words, force fields are written in the language of Newtonian forces, rather than chemical reactivities, and thus it is these physical forces (rather than their chemical basis) that are explicitly used to determine system dynamics. In contrast to these physical force field descriptions, the methods presented in this section employ primarily chemical descriptions of systems, with chemical reactivity providing the driving force for exploring the chemical dynamics of a system. The primary advantage of turning from a physical to a chemical description of a reactive system is quite simple. The vast majority of physical processes and events (e.g., collisions, rotations and vibrations) are not reactive events (i.e., chemical processes) and thus in and of themselves are of no interest for obtaining a chemical description of a system. Yet because of their enormous frequency (often many orders of magnitude greater) compared with chemical events, the vast majority of the computational resources required for a physical simulation of a system are used to simulate uninteresting physical processes. Only a very small fraction of the employed resources are then actually used to directly simulate the reactive events of interest. A chemical

description of a system, on the other hand, only considers chemical processes explicitly and thus avoids the tremendous expense of explicitly simulating uninteresting physical processes.

1.5.2 Chemical Kinetics

A chemical description of a system is typically given in terms of discrete chemical states, which are connected by chemical reactions. Mathematically, this means that a chemical system can be modeled by a so-called Markov process. The dynamics of such a system (i.e., a system limited to discrete states with probabilistic rules governing the transitions between these various states) is governed by the so-called Master equation:

$$\frac{\mathrm{d}P(\sigma)}{\mathrm{d}t} = \sum_{\sigma' \neq \sigma} P(\sigma') W(\sigma' \to \sigma) - \sum_{\sigma' \neq \sigma} P(\sigma) W(\sigma \to \sigma')$$
(1.60)

System states are denoted as σ , and the probability of finding the system in a particular state, σ , is $P(\sigma)$. The probability per unit time of a transition from state σ to state σ' (assuming the system is initially found in state σ) is represented by $W(\sigma \rightarrow \sigma')$. If the system can be broken down into a collection of lattice sites with index *i*, then the overall state of the system can be written as a conjunction of the states of the individual sites and the evolution of the state of a particular site *i* can be written as:

$$dP(\sigma_i) = \sum_k w_{ik}^+(\sigma)dt - w_{ik}^-(\sigma)dt$$
(1.61)

where k is an index over all processes leading to or from the σ -state and where the transition probabilities, w_{ij} , for the processes are functions of the overall state of the system. The Master equation, in either form, is deterministic; however, its high dimensionality makes an analytical solution impossible to find for all but the most trivial systems, and the vast number of states and processes to consider makes a deterministic, numerical solution equally impractical in most cases. Thus stochastic methods are typically employed to simulate the chemical dynamics described by the Master equation. The remainder of this section is devoted to describing how a family of approaches, known as kinetic Monte Carlo (kMC) methods, can be employed to provide stochastic solutions of the Master equation.

1.5.3 Kinetic Monte Carlo

Kinetic Monte Carlo methods extend the time scale of reactive simulations by using statistical mechanics to fast forward the dynamics to the next reactive event, rather than explicitly simulating long periods of quasi-equilibrium dynamics between reactions [67–70].

1.5.3.1 System States and the Lattice Approximation

In order to apply the Master equation to a chemical system we must first characterize it in terms of discrete states. For crystal structures or surfaces the lattice





Figure 1.16 Schematic representation of typical processes included in kMC models: adsorption, desorption and diffusion.

approximation provides an easy and intuitive way of doing this. In the lattice approximation the system is spatially divided into discrete sites, with each site being allowed to be either wholly unoccupied or occupied by one of the possible chemical species present in the system. Typically, three types of processes, the first two of which are illustrated in Figure 1.16, are then considered. First, adsorption/ desorption of a species at a site. Second, diffusion of an adsorbate from one site to an adjacent site. Third, reactions between species on adjacent sites. The reactive events involve two neighboring sites at most, or perhaps just one site and an implicitly included gas or liquid phase molecule. As a result only the local configuration (i.e., the state of nearby sites) is necessary for determining which reactive processes are possible at a given lattice site. The main disadvantages of the lattice approximation are that it is only applicable to strictly crystalline or crystal-like systems, and that it typically only allows for simple species and processes involving at most one or two lattice sites. To avoid these disadvantages, off-lattice kMC approaches have been developed [71-74]. Nevertheless, the vast majority of kMC calculations still make use of the lattice approximation.

1.5.3.2 Reaction Rates

Once the discrete states of the system have been defined the possible transitions between these states and their corresponding transition rates need to be determined. Within the on-lattice approximation, reactions typically only involve one or two lattice sites directly and are typically only influenced by the states of nearby sites (rather than the configuration of the entire system). As such, all possible reactions are easily categorized into a much smaller number of prototypical reactions, each of which has an associated reaction rate which is valid for all reactions of its type. The rates of these prototypical reactions are then extracted from either experimental data or higher level calculations making use of transition state theory, as discussed in Section 1.3.3.3. The use of an electronic structure or reactive force field method to obtain the reaction parameters needed to define a kMC model is a good example of a multiscale model that can be developed using either serial or concurrent coupling [75]. In the serial-coupling approach all reaction parameters needed to fill in a preconceived reaction table (whose contents are determined by the developer)

and obtained from the higher level method independent of the kMC model they are used to parametrize. The primary benefit of this approach is the simplicity of its implementation. In contrast, concurrent-coupling approaches try to take advantage of automated reaction and transition state search algorithms to locate and characterize reactions on-the-fly, that is, during the course of a kMC simulation. The possibility of discovering novel reactions or reaction pathways has thus far been the primary motivation for the development of on-the-fly methods [71,76]. Another possible benefit for systems with large numbers of possible reactions would be the computational savings resulting from only calculating the barriers for reactions actually needed to run the kMC simulation rather than all conceivable reactions.

1.5.3.3 Reaction Dynamics

Now that the system states and probabilities of transitions between states have been determined, it remains to be discussed how to stochastically step from one state to another in such a way that the reactive dynamics of the system are meaningfully



Figure 1.17 Flow charts showing typical kMC schemes based on null-event (a) and rejection-free (b) algorithms.

modeled. Given an initial state of the system, there are two basic strategies for selecting the reactive event that should lead to the next system state (see Figure 1.17).

In null-event algorithms (e.g., the well known Metropolis algorithm [77]) a site is randomly selected (with each site having an equal probability of being selected) and the probability, w_i , for each possible reaction at the site is computed (or looked up in a reaction table). These probabilities are then normalized using the total reaction probability, w_{tot} , for the most reactive site possible in the system (note that w_{tot} is computed once at the beginning for the simulations and then remains constant throughout the simulation, regardless of which site is currently being sampled). Thus, the sum of the normalized probabilities, $k_i = \frac{w_i}{w_{tot}}$, for the reactions associated with the selected site is less than one. A random number, x, is now generated and the *j*th process is selected for execution when:

$$\sum_{i=1}^{j-1} k_i < x \le \sum_{i=j}^n k_i$$
(1.62)

If $x > \sum_{i} k_i$ no event takes place. Otherwise, the system is updated in accordance

with the event which has been carried out before the simulation proceeds to the next step, where another site is selected and an event associated with this site is carried out if the Monte Carlo procedure described above (i.e., the comparison of the process probabilities with a new random number) is met. Thus, the cycle of steps continues until the desired number of iterations or reactive events has been reached. A major advantage of a null-event algorithm is that the reaction rates for only a very limited number of precesses need to be computed at each iteration. Thus null-event algorithms are well suited for being concurrently coupled with a higher level of theory, which calculates the required reaction barriers and rates as needed on-the-fly. However, a major disadvantage of null-event algorithms can be that not every step results in a successful event. Thus there are wasted Monte Carlo steps, whose computational expense does not contribute directly to advancing the reaction dynamics of the system. In contrast, rejection-free algorithms execute a reactive process at every Monte Carlo step; however, the price they pay for this is that the probability of every process must be taken into account at every step. A typical rejection-free algorithm proceeds as follows. The probability, w_i , of every possible process that the system in its current state might undergo is calculated (or looked up in a table) and these are summed to give a total probability or reaction rate for the entire system:

$$w_{\text{tot}} = \sum_{i=1}^{n} w_i \tag{1.63}$$

This total probability is then used to normalize the individual probabilities and a random number is used to choose one of these, as in the case of the null-event algorithm. However, here, because the sum of the normalized probabilities is exactly one, an event is guaranteed to occur. An additional advantage of rejection-free algorithms is that each kMC iteration can be converted into real time based on the rates for all possible reactions in the system. If the rates, w_i , of all possible reactions (i.e., all reactions that might be chosen) in the system are known, then there

is a direct connection between the kMC iteration and real time, such that real time is advanced by Δt at each iteration:

$$\Delta t = \frac{-\ln(x)}{\sum\limits_{i=1}^{n} w_i} \tag{1.64}$$

where *x* is a random number between 0 and 1 [78]. All that now remains is to update the system based on the executed event. This entails changing the state of affected lattice sites and the reaction processes and rates associated with them along with the overall system rate. Because only a small fraction of the system has typically been affected by the occurrence of a single process it is typically more efficient to only update these parts of the system, rather than the system as a whole. In any case, a variety of data structures, ranging from simple arrays or lists to binary trees, can be chosen to better facilitate the efficient or convenient search (e.g., simple linear, n-level linear or binary) and update (e.g., local vs global) strategies [69].

1.5.3.4 Applications of kMC in Electrochemistry

The lattice approximation makes kMC particularly well suited for simulations of crystal growth [79], making it an obvious choice for simulations of metal deposition under electrochemical conditions [15]. For similar reasons it is sometimes well suited for studies of surface catalysis [80]; however, the large number of possible surface reactions coupled with the possibility of adsorbates occupying more than one surface site can make such applications somewhat cumbersome and involved.

Finally, a common difficulty with kMC should be mentioned. The original goal of the kMC method was to separate fast uninteresting physical processes (such as vibrations) out of the dynamics and leave only interesting chemical processes implicitly in the simulations. Unfortunately, for many surface simulations the vast majority of kMC processes are simple diffusion steps, which in and of themselves are not very interesting. Various approaches to further accelerate kMC simulations have been developed [69]; however, the first passage method, which separates out and effectively fast forwards diffusion by wrapping up collisionfree diffusion processes into single Monte Carlo events is particularly worth mentioning [81].

1.5.4 Summary

This section began by recounting the role of the Master equation in chemical kinetics theory. A common approach to stochastically propagating the dynamics prescribed by the Master equation is the use of kinetic Monte Carlo methods. Traditionally kMC simulations make use of pre-defined reaction tables of allowed chemical events and the lattice approximation, which restricts all species to discrete lattice sites. Thus, kMC is particularly well suited for crystal growth and metal deposition simulations. Nevertheless, the development of off-lattice and on-the-fly kMC approaches opens the door to more exotic applications as well.

1.6

The Oxygen Reduction Reaction on Pt(111)

1.6.1

Introduction to the Oxygen Reduction Reaction

The oxygen reduction reaction (ORR) is a fundamental electrochemical reaction which plays a critical role in such varied phenomena as combustion, corrosion and cell respiration, and finds application in many energy conversion and/or storage technologies [82–85]. Of particular interest is its central role in powering polymerelectrolyte (or proton-exchange) membrane fuel cells (PEMFCs), which is driving the search for improved ORR catalysts. One of the most commonly used ORR catalysts is Pt(111). Although the ORR on Pt(111) should ideally generate 1.23 V per electron (see Figure 1.18), an operating potential of at most 0.90 V is experimentally realized. A detailed atomistic-level understanding of the ORR mechanism on Pt(111) could provide important insights toward understanding the cause of this ~ 0.3 V over-potential and developing strategies to reduce or eliminate it.

In this section we highlight an application of some of the techniques discussed in the previous sections to study the mechanism of the ORR on Pt(111). Concurrent coupling between DFT, which is at the heart of the approach presented here, and a Poisson–Boltzmann continuum solvation model are employed to obtain a detailed picture of the relevant energy landscape. Eyring's canonical transition state theory is then used, by way of serial coupling, to develop a kinetic rate model of the system.

1.6.2

Preliminary Considerations

Before applying any of our methods to this system, it is important to think through exactly what we want to model and what appropriate starting points or initial guesses we need to pursue. In this case, the reaction we want to model (shown in Figure 1.18) involves breaking an O-O bond and forming four O-H bonds, two to each O atom. Now we might begin by asking in which order these five individual steps take place. In other words, when does the O-O bond break and when do the O-H bonds each form? The first possibility is that the O-O bond dissociation might take place before any O-H bonds are formed. In this case O_2 is the dissociating species

$$2 H_{2(g)} \longrightarrow 4 H_{(aq)}^{+} + 4 e^{-} \qquad E^{\circ} = 0 V \text{ (anode)}$$

$$O_{2(g)} + 4 H_{(aq)}^{+} + 4 e^{-} \longrightarrow 2 H_2O_{(l)} \qquad E^{\circ} = 1.229 V \text{ (cathode)}$$

$$2 H_{2(g)} + O_{2(g)} \longrightarrow 2 H_2O_{(l)} \qquad E^{\circ} = 1.229 V$$

Figure 1.18 Hydrogen oxidation (anode) and oxygen reduction (cathode) at fuel-cell electrodes.

and so we name this the O_2 -dissociation mechanism. The second possibility is that a single H is added to O_2 to form OOH before O—O bond dissociation, so that OOH is the dissociating species. We call this mechanism the OOH-dissociation mechanism. Finally, if a H is added to each O to form HOOH before the O—O bond dissociates, then we call this a H₂O₂-dissociation mechanism. The addition of more than one H to either O prior to O—O bond dissociation is not considered because it would involve either over-filling the valency of oxygen (even if we ignore bonding to the surface) or require simultaneous dissociation of the O—O bond, both of which seem unlikely. Thus, we consider these three general reaction mechanisms, which are illustrated in Figure 1.19.

Because the ORR is catalyzed by the Pt(111) surface, we expect its critical step(s) to involve adsorbates. Thus, we anticipate that the O—O bond cleavage takes place on the Pt(111) surface, along with the H-addition steps. While this means that the oxygen species being protonated is expected to be adsorbed to the catalyst surface throughout the reaction, there are two possible immediate sources for the protons added during the H-addition steps. These might either first adsorb to the Pt(111) surface and then react with the oxygen species, or the protons might come directly from the electrolyte and thus never adsorb to the surface directly. The former type of reaction is known as a Langmuir–Hinshelwood-type (LH-type) reaction, and the latter as an Eley–Rideal-type (ER-type) reaction. A schematic of these is presented in Figure 1.20. Both cases should be considered within each of the three dissociation



Figure 1.19 Schematic representation of the three investigated ORR mechanisms. Highlighted with a red box and red arrows is the O_2 dissociation mechanism, in blue the OOH dissociation mechanism and in green the HOOH dissociation mechanism. The black

arrows denote the subsequent reactions after the first O—O bond dissociation. A star denotes a coupled proton electron transfer (CPET) process, which can take place through either a LH-type or ER-type mechanism.



Figure 1.20 Schematic representation of Langmuir–Hinshelwood (LH)- and Eley–Rideal (ER)-type reaction mechanisms.

mechanisms discussed above, and, indeed, both have been considered [86,87], however, we will limit most of our discussion here to LH-type reactions.

1.6.3 DFT Calculations

The geometries for the reactants, products, intermediates and transition states involved in each dissociation pathway were optimized within a DFT description of the system. In particular, the B3LYP flavor of DFT [88-91] in conjunction with an LACVP** basis set [92-96] was used as implemented in the Jaguar program [97] to calculate the energies and forces involved in obtaining the optimal geometry for each system state, and it corresponding "raw" system energy, E^{SCF}. In all cases, not only converged energies and geometries, but also converged spin states are used in arriving at the final computed energies, a detail which is often essential for accurately reproducing experimental results [98]. Using an appropriate model for the electrode surface is even more vital for reliable calculations; however, the development of such a model can be an arduous task [86, 99-101]. The results presented in this section were obtained using a Pt₃₅ cluster model. The cluster contains three layers of atoms, most of which are fixed at their experimental bulk positions. Only four atoms in the center of the (111) surface are allowed to relax. Although this cluster is significantly larger than many of the metal clusters commonly used to model catalytic surface reactions, extensive cluster-size convergence studies have shown that a 3-layer Pt₂₈ cluster is the smallest, shallowest cluster

capable of reliably reproducing adsorption energies [99]. The Pt_{35} cluster has been shown to provide a reliable model for an extended Pt(111) surface, such as is found on a Pt electrode.

1.6.4 Method Validation

While computational convergence demonstrates a level of consistency within our DFT model, it is unable to identify systematic errors which might invalidate converged results. Thus, it is good practice to check a new model/level of theory by comparing results obtained using it to experimental results. The binding energies of O, O₂ and H₂O to Pt(111) under low-coverage, low-pressure and low-temperature conditions have been measured experimentally using thermal desorption spectroscopy (TDS) [102-104] and electron energy-loss spectroscopy (EELS) [105-107], and found to be in the ranges 3.47-3.73 eV, 0.3-0.5 eV, and 0.43-0.65 eV, respectively. The O₂ dissociation barrier has also been measured to be in the range 0.3–0.5 eV and STM imaging shows that while O₂ preferentially binds at a bridge site, dissociation involves a different intermediate binding site. Using the DFT methods and models presented directly above, the binding energies for O, O₂ and H₂O were calculated to be 3.25, 0.49 and 0.60 eV, respectively and O₂ is found to have a dissociation barrier of 0.65 eV, which involved migration to an fcc site. Thus, the experimental results are well reproduced within an acceptable degree of accuracy by the theoretical approach taken here. Unfortunately, a direct comparison under electrochemical conditions is not yet possible because traditional ORR experiments measure overall activity rather than individual binding energies.

1.6.5 Reaction Energies

Based on the raw SFC energies (E^{SCF}) computed for relevant reactants, products, intermediates, transition states, and reference molecules using the methods and model outlined above, reaction energies and barriers can be computed for each step in the three ORR reaction mechanisms considered here. Gas phase H₂, O₂ and the bare Pt₃₅ cluster are taken as reference states, so that the reaction energy (ΔE_{gas}) associated with each reactant, product, intermediate or transition state is calculated as follows:

$$\Delta E^{\text{gas}} := E^{\text{SCF}}_{\text{sys}} - E^{\text{SCF}}_{\text{Pt}_{35}} - \frac{1}{2} N_{\text{H}} E^{\text{SCF}}_{\text{H}_2} - \frac{1}{2} N_{\text{O}} E^{\text{SCF}}_{\text{O}_2}$$
(1.65)

These energies are plotted in Figure 1.21, which shows the energetics of three different ORR mechanisms using the LH mechanism for all H-addition steps. Excepting the removal of water at the last step, all individual reaction steps (in all three mechanisms) are downhill. Nevertheless, there are barriers to slow down the kinetic rates of many steps. Thus, the initial dissociation of O—O has a barrier of



Figure 1.21 Energy profiles of LH-type mechanisms for the surface ORR under gas phase conditions. Only the adsorbates containing O atoms are denoted for clarity. Unlabeled potential energy wells correspond to the preceding intermediate $+H^*$.

0.65 eV, and the addition of a first H to O to form OH via a LH-type mechanism is the largest barrier: 1.25 eV. The barrier for H-addition to form H₂O is small (0.24 eV), and desorption of the final product (H2O) has a similar barrier (0.60 eV, which is the same as the reaction energy in this case) to the initial O-O bond dissociation step. Thus, the addition of an initial H to a lone O to form OH is the rate-limiting reaction within the O2-dissociation mechanism. The OOH mechanism introduces a new H-addition step at its commencement ($O_2 + H \rightarrow OOH$), whose barrier is negligible (0.05 eV). The subsequent OOH dissociation step (OOH \rightarrow O + OH) has a barrier (0.74 eV) which is slightly higher than the dissociation barrier in the O2 dissociation mechanism. Subsequent steps follow the same pathway as is found in the O2 dissociation mechanism, and so once again the H-addition to form OH is the reaction step with the highest barrier (1.25 eV). The H₂O₂-dissociation mechanism avoids this high-barrier step by adding an H to each O in O₂ before the O—O bond is cleaved. The barrier for adding this second H to form HOOH using a LH mechanism is 0.47 eV, and is almost identical to the subsequent barrier for breaking the O—O bond in the thus formed H_2O_2 . Thus, the energy required to desorb the final product (H2O) from the surface (0.60 eV) is the highest barrier for this mechanism. Because it is less than half the value of the highest barriers in the other two mechanisms, we anticipate that the H2O2 dissociation mechanism will dominate under these conditions (i.e., zero pressure and temperature and no zeropoint-energy effects!). As should be evident from the conditions mentioned above, there are a number of factors which need to be corrected for before applying our model to electrochemical systems. These include solvation effects, free energy contributions, and the electrode potential. We now explain the inclusion of each of these in turn.

1.6.6 Solvation Effects

Solvation energies were calculated using an implicit solvation model. The solvent molecules are modeled as a continuous dielectric material, surrounding a cavity, specifically fitted to the solvated molecule(s). Assuming a Boltzmann-type distribution of solvent ions, the Poisson–Boltzmann equation gives the electrostatic potential in terms of which the interaction energy between the solvent and solute can be computed using:

$$\nabla[\varepsilon(\mathbf{r}) \cdot \nabla V_{\rm es}(\mathbf{r})] = -4\pi \left[\rho^f(\mathbf{r}) + \sum_i c_i^\infty z_i \lambda(\mathbf{r}) \exp\left(\frac{-z_i V_{\rm es}(\mathbf{r})}{k_{\rm B} T}\right) \right]$$
(1.66)

The terms in the above Poisson–Boltzmann equation are the following: $\varepsilon(\mathbf{r})$ is the dielectric constant of the solvent, V_{es} is the electrostatic potential, $\rho^f(\mathbf{r})$ is the charge density of the solute, c_i^{∞} is the bulk concentration of solvent ion-type *i*, which has a net charge of z_i and $\lambda(\mathbf{r})$ is the accessibility that the solvent has to position \mathbf{r} . The free energy of solvation is then the sum of the energy required to form the solute cavity in the dielectric and the energy required for charging the solvent near the cavity surface. The solvation energy was thus calculated using the Jaguar [97] Poisson–Boltzmann solver for each step of the SCF energy procedure and included in the SCF energy at each iteration. Nevertheless, the solvation energy (E^{solv}) is easily extracted again, so that reaction energies, which now include solvation effects can be written as:

$$\Delta E^{\text{solv}} = E^{\text{gas}} + (E^{\text{solv}}_{\text{products}} - E^{\text{solv}}_{\text{reactants}})$$
(1.67)

These solvation energies are plotted in Figure 1.22. There we see that solvation dramatically increases the attraction of O_2 to the surface, so that the adsorption of O_2



Figure 1.22 Energy profiles of LH-type mechanisms for the surface ORR under the influence of implicit water solvation. Only the adsorbates containing O atoms are denoted for clarity. Unlabeled potential energy wells correspond to the preceding intermediate $+H^*$.

is now -1.71 eV (instead of -1.05 eV) downhill. The barriers for O—O dissociation (0.69 eV instead of 0.65 eV) and the first H-addition steps (1.14 eV instead of 1.25 eV) show only minor changes. On the other hand, the barrier for water formation increases dramatically (1.10 eV instead of 0.24 eV) and is now uphill with a reaction energy of 0.24 eV (was -1.05 eV downhill). Finally, the desorption of water is more uphill than it previously was (0.83 eV instead of 0.60 eV). Although the inclusion of solvation effects dramatically changes some of the barriers, the initial H-addition step still has the highest barrier, which has undergone only a small decrease.

Similar trends are observed when we consider the effects of solvation on the OOH-dissociation mechanism. The first H-addition step (OOH formation) is now uphill (0.22 eV instead of -0.60 eV) and has a significant barrier (0.94 eV instead of 0.05 eV). In contrast, the OOH-dissociation barrier remains relatively unchanged (0.62 eV instead of 0.74 eV). Thus OH formation remains the process with the highest barrier (1.14 eV instead of 1.25 eV) following the inclusion of solvation effects.

In the case of the H_2O_2 -dissociation mechanism, we once again see solvation primarily resulting in increased H-addition barriers, while leaving the O—O bond dissociation step relatively untouched. Thus the second H-addition to form H_2O_2 is an uphill reaction when solvated and now has the highest barrier within the mechanism (1.23 eV instead of 0.47 eV), while the H_2O_2 dissociation barrier remains almost constant (0.43 eV instead of 0.46 eV).

Thus, now that solvation effects have been included the H_2O_2 -dissociation mechanism has the highest overall barrier (1.23 eV vs. 1.14 eV for each of the other two mechanisms) instead of the lowest, as was the case before including solvation (0.60 eV vs. 1.25 for each of the other two mechanisms).

1.6.7

Free Energy Contributions

Free energies were calculated within an ideal gas approximation. Vibrational states (i.e., normal modes) were extracted from the Hessian of each structure and then used to calculate the zero-point-energy correction (E^{ZPE}) the temperature-dependent enthalpy correction, H(T), and the temperature-dependent entropy, S(T). The Gibbs free energy in solvent, ΔG_T^{solv} , was then calculated as:

$$\Delta G_T^{\text{solv}} := \Delta E^{\text{solv}} + \Delta E^{\text{ZPE}} + \Delta H_T^{\text{vib}} - T\Delta S_T^{\text{vib}}$$
(1.68)

where ΔE^{solv} , ΔE^{ZPE} , ΔH_T^{vib} and ΔS_T^{vib} indicate the difference of these respective quantities between the products and reactants under consideration. The Gibbs free energy for the three LH reaction mechanisms at 298 K are shown in Figure 1.23.

The inclusion of these thermal contributions decreases the favorability of O_2 dissociation substantially from 1.71 to 1.35 eV; however, the barrier is unchanged (0.68 eV). The OH formation reaction energy and barrier both show similar small increases (from 0.0 to 0.20 eV and from 1.14 to 1.19 eV, respectively). A similar trend is also observed for H₂O formation as the overall reaction energy increases from



Figure 1.23 Energy profiles of LH-type mechanisms for the surface ORR under gas phase conditions. Only the adsorbates containing O atoms are denoted for clarity. Unlabeled potential energy wells correspond to the preceding intermediate $+H^*$.

0.24 to 0.55 eV and the reaction barrier from 1.10 to 1.27 eV. Thus, with the inclusion of thermal contributions at 298 K, the highest barrier in the O₂-dissociation mechanism is 1.27 eV, which is associated with H₂O formation.

In the OOH-dissociation mechanism H-addition is also somewhat inhibited by the inclusion of thermal contributions at 298 K. Thus, the overall energy and reaction barrier for OOH formation increase from 0.22 to 0.52 eV and from 0.94 to 1.09 eV, respectively. As was also the case in the O₂-dissociation mechanism, the dissociation step in the OOH-dissociation mechanism is left essentially unaffected (the barrier is lowered from 0.62 to 0.59 eV). Thus, again, the formation of water is now the step with the highest barrier (1.27 eV).

Finally, the inclusion of thermal contributions to yield free energies for the H_2O_2 -dissociation pathway increases the second H-addition step needed to form H_2O_2 from 1.23 to 1.46 eV, so that it remains the step with the highest reaction barrier. As was seen in the other mechanisms, the O—O bond dissociation step (here H_2O_2 dissociation) only changes slightly as it is reduced from 0.43 to 0.31 eV.

1.6.8

Influence of an Electrode Potential

Thus far we have not considered the influence of the electrode potential. As mentioned in Section 1.3.4.3, the electrode potential can be modeled to a first order of approximation by multiplying the electrode potential by the number of electrons transferred at each electron-transfer step. In our ORR mechanisms an electron is transferred to the surface every time a H atom leaves the electrolyte solution phase and electrically attaches to the surface, either by adsorbing directly (as is the case within LH-type mechanisms) or by bonding to another molecule which is already adsorbed to the surface (as in the case in ER-type mechanisms).

Results at zero potential (U=0.0 V vs. the reversible hydrogen electrode, RHE) and the ideal electrode potential (U=1.23 V vs. the RHE) are summarized in Figure 1.24a and b, respectively. Here we have included both the LH- and ER-type mechanisms to illustrate how turning to an ER-type mechanism can be used to avoid the large H-addition barriers present in the LH-type mechanisms at zero potential.

At zero potential the overall ORR process is downhill -4.57 eV. The LH-type reaction barriers are rate limiting in all LH-type pathways and range from 1.09 to 1.19 to 1.28 to 1.46 eV for the formation of OOH, OH, H₂O and H₂O₂, respectively.



Figure 1.24 Electrochemical ORR mechanism at (a) U = 0.0 V and (b) U = 1.14 V vs. RHE (calculated equilibrium potential). The LH steps are denoted by dashed lines and the ER steps by dotted lines.

The corresponding reaction barriers for the addition of a proton taken directly from the electrolytic phase in the ER-type pathways are all much lower (approximated to be 0.3 eV for downhill reactions) [86]. Thus one would expect ER-type pathways to dominate at low potentials.

At the ideal potential, the overall ORR process is now energetically neutral $(\Delta G(298) = 0)$. While the relative energies of intermediates in the LH-type mechanisms change, the barriers remain unaffected (only the reverse barriers are affected within our model) by the application of the electrode potential. In contrast, the barriers for the ER steps in the ER-type mechanisms increase significantly, since the barriers here are calculated relative to the products rather than relative to the reactants, as is the case for LH-type reaction steps. Thus the H-addition barriers for the formation of OOH, H₂O₂, OH and H₂O via ER-type processes are now 1.15, 1.16, 0.87 and 0.99 eV, respectively. As a result LH-type mechanisms are expected to be competitive with ER-type processes at similar potentials and among the ER-type mechanisms, the H₂O₂-dissociation pathway is expected to dominate as its highest barrier is 0.15 eV lower than the highest barrier for each of the other two mechanisms.

1.6.9 Modeling the Kinetic Rates

To better understand the phenomenological implications of these free energy landscapes, we take advantage of a simple kinetic model to describe the competition between the investigated ORR mechanisms. At the heart of this kinetic model is Eyring's canonical transition state theory (see Section 1.3.3.3 for more details) [24,87], which enables us to convert the reaction barriers acquired using DFT into kinetic rates. Thus the relationship between the DFT calculations and the kinetic model is a straightforward example of serial coupling. The kinetic model utilized here, takes two types of processes into consideration: those which end in surface O or OH (i.e., adsorption and dissociation processes), and those which remove OH from the surface (i.e., H_2O formation and desorption) or lead away from its formation (desorption of H_2O_2). Thus, the three ORR mechanisms investigated using DFT are broken down into the following six processes (shown in Figure 1.25) which we label as: O_2 -dissociation, OOH-dissociation, HOOH-dissociation, HOOH desorption, and H_2O formation (starting from either O or OH).

The rate of each of these five processes is assumed to correspond to the rate of the slowest step in it (i.e., the step with the highest barrier), and the concentration of reactants leading up to each of these bottleneck barriers is assumed to be one for the sake of making a simple comparison between pathways. Thus, the rate constant for each of the six processes is found using Eyring's equation:

$$k(U) = \frac{k_{\rm B}T}{h} \exp\left[\frac{-\Delta G_T(U)}{k_{\rm B}T}\right]$$
(1.69)

where $k_{\rm B}$ is Boltzmann's constant, *T* is temperature, *h* Planck's constant, and $\Delta G_T(U)$ is the potential-dependent barrier.

Incoming Processes

O2- dissociation mechanism (kO2)

$$O_2 \xrightarrow{-1.35} O_2^* \xrightarrow{-1.71} O_2^* + O_2^*$$

OOH - dissociation mechanism (k_{OOH})

$$O_2 \xrightarrow{-1.35} O_2^* \xrightarrow{-0.42} OOH^* \xrightarrow{-2.03} OH^* + O^*$$

HOOH - dissociation mechanism (k_{HOOH})

$$O_{2} \xrightarrow{-1.35} O_{2}^{*} \xrightarrow{-0.42} OOH^{*} \xrightarrow{-0.26} HOOH^{*} \xrightarrow{-2.51} OH^{*} + OH^{*}$$

$$(eU - 0.42) + 0.30 U < 0.42 (eU - 0.26) + 0.30 U > 0.26$$

Outgoing Processes

HOOH - desorption (k_{HOOH, off})

H₂O - formation/desorption (k_{H2O,O})

$$O^* + H^* \xrightarrow{-0.34} OH^* \xrightarrow{-0.39} + 0.30 U < 0.34$$

(eU - 0.34)+0.30 U > 0.34 (eU - 0.39)+0.30 U > 0.39 H₂O^{*} \xrightarrow{-0.38} H₂O

H₂O - formation/desorption (k_{H2O,OH})

$$OH^* \xrightarrow{-0.39} +0.30 \ U < 0.39 +0.30 \ U > 0.39 H_2O^* \xrightarrow{-0.38} +0.38 H_2O$$

Figure 1.25 Reaction schemes for single rate processes considered in kinetic rates analysis. Reaction energies (italics) and barriers (bold) are given in eV above and below the reaction arrows. The electrode-potential dependence for the reaction energies and barriers of CPET

processes are given by including the appropriate correction as a function of the electrode potential, *U*, in the energy expression. The potential-dependent rate constants for these kinetic processes are plotted in Figure 1.26.

The incoming phase of the O₂-dissociation mechanism (k_{O_2}) includes no CPET processes, so that its rate is independent of the electrode potential. The highest barrier is for the O₂-dissociation step, 0.68 eV, making this the slowest incoming process at low potentials. As two O adatoms are the final products for this process, the outgoing process required to complete the O₂-dissociation mechanism is the formation of water from an O adatom. ($k_{H_2O,O}$).

The incoming phase of the OOH-dissociation mechanism (k_{OOH}) includes a single CPET process. At low potentials this CPET process is downhill and thus only has a small barrier of 0.30 eV, leaving the potential-independent dissociation step to be the rate-determining process with a barrier of 0.59 eV. However, once the electrode potential reaches U = 0.42 V the CPET barrier begins to increase with the increasing potential and overtakes the dissociation to become the rate-limiting

step at U = 0.71 V. The overall rate for the incoming portion of the OOH-dissociation mechanism is now potential-dependent and is slowed down by further increases in potential. The result of the incoming portion of the OOH-dissociation is a mixture of O adatoms and adsorbed OH. To avoid a build-up of O adatoms on the surface, which could ultimately disable the cataylitic properties of the surface by blocking cataytic sites, the entire water formation pathway starting from an O adatom ($k_{H_2O,OH}$) and not just the second portion starting from OH ($k_{H_2O,OH}$) is needed to make the OOH mechanism a viable catalytic pathway.

The incoming phase of the HOOH-dissociation mechanism is similar to that of the OOH-dissociation mechanism except that it incorporates an additional CPET step and has a significantly lower dissociation barrier (0.31 eV). This dissociation barrier is, nevertheless, still seen to be rate limiting at low potentials (although the difference between 0.30 and 0.31 is within the uncertainty of our methods). The second CPET step is less favorable than the first and so its potential dependence is triggered at U = 0.26 V and comes into play almost immediately (at U = 0.27 V) to make it the ratelimiting step. As OH is the sole product of the incoming portion of the HOOHdissociation mechanism, only the shorter H₂O formation/desorption pathway is needed to arrive at the desired product. However, the desorption of H₂O₂ provides a second possible outgoing pathway ($k_{H_2O_2,off}$), leading to undesired products (H_2O_2). This desorption process is itself potential-independent, but does depend on the potential-dependent formation of HOOH for the formation of its necessary reactant. Any HOOH* which is formed can then either dissociate, with a barrier of 0.31 eV, or desorb, with a barrier of 0.34 eV. Because these barriers are similar, we anticipate that any utilization of the HOOH pathway will result in a mixture of desired H₂O and undesired H₂O₂ products. However, at potentials above 0.5 eV the slowdown in the CPET processes needed to remove OH from the system may result in OH overcrowding on the surface, which would encourage H₂O₂-desorption.

The two outgoing processes, which form H₂O from O and OH, respectively ($k_{H_2O,O}$ and $k_{H_2O,OH}$) consist of one or two CPET steps followed by H₂O desorption. At low potentials the potential-independent desorption barrier of 0.38 eV is rate limiting; however, the first CPET step in each process becomes rate limiting at U = 0.43 V and U = 0.47 eV, respectively. Thus for potentials greater than U = 0.43 V, H₂O formation starting from O is slower than starting from OH.

The potential-dependent rate constants for each of these six processes at 298 K are plotted in Figure 1.26. At low potentials the incoming rate for HOOH formation and dissociation (k_{HOOH}) is the fastest process. The outgoing processes relevant to the HOOH and OH formed ($k_{H_2O_2}$ and $k_{H_2O,OH}$ respectively) are one half and a whole order of magnitude slower than the incoming reaction sequence, suggesting that OH is likely to build up on and poison the surface at low potentials. At U=0.27 V k_{HOOH} begins to decrease and drops below the outgoing processes, which form H₂O₂ (($k_{H_2O_2}$) and H₂O ((k_{H_2O}), at U=0.30 V and U=0.34 V, respectively. Until k_{HOOH} crosses k_{OOH} at U=0.55 V, the HOOH-dissociation mechanism is the dominant incoming pathway and should result in a mixture of H₂O₂ and H₂O products. As the OOH-dissociation mechanism becomes the dominant incoming pathway the production of H₂O relative to that of H₂O₂ should increase, and the



Figure 1.26 Potential-dependent rate constants corresponding to different ORR mechanisms. Rate constants k_{O_2} , k_{OOH} , and k_{HOOH} correspond to the smallest calculated rate constant for each mechanism ending with O-O, O-OH, and HO-OH dissociations, respectively. The rate constant k_{out} corresponds to the smallest calculated rate constant to create H₂O from O and/or OH intermediates. $k_{H_2O_2,off}$ corresponds to the rate constant for

desorbing H_2O_2 from the Pt(111) electrode. The vertical axis is a measure of the relative magnitude of the rate constants. Solid lines represent ingoing mechanisms for species that adsorb onto the surface; dashed lines correspond to mechanisms that lead to the removal of surface-adsorbed species. The reaction pathways, reaction energies and barriers corresponding to each of the process rates are presented in Figure 1.25.

surface should remain relatively free from blockage (due to outgoing processes having faster rates than incoming processes) up to U = 0.63 V and U = 0.68 V, at which points O and OH, respectively, are expected to begin to accumulate on the surface. Nevertheless, the downward turn of k_{OOH} shortly thereafter may keep the incoming and outgoing rates similar enough to support efficient catalytic activity. At U = 0.72 V, U = 0.77 V and U = 0.80 V $k_{H_2O,O}$, $k_{H_2O,OH}$ and k_{OOH} , respectively, drop below k_{O_2} , leaving O₂-dissociation to be the dominant process for potentials above U = 0.80 V. Thus we anticipate the accumulation of oxygen on the surface at these high potentials.

1.6.10 Summary

To illustrate some of the approaches and methods presented in earlier sections, this section has summarized a computational study of the ORR on Pt(111). Three dissociation mechanisms were investigated with DFT, and both LH- and ER-type H-addition processes were considered within each mechanism. A Pt₃₅ cluster was used to model the electrode surface. All reactions were first studied in a gas phase environment before the inclusion of an aqueous solvent by means of a Poisson–Boltzmann continuum model. The inclusion of solvent significantly changed the energetics of several reaction steps;

however, the same steps remained rate determining and these were hardly affected. Based on normal modes extracted from the Hessian of each structure, free energies at 298 K were calculated within the ideal gas approximation. The inclusion of these free energy corrections resulted in a scenario in which water formation became the highest barrier in two of the three mechanisms. The influence of an electrode potential showed that at high potentials LR-type reaction pathways are competitive with ER-type pathways, which are strongly preferred at low potentials. Finally, a kinetic rate model was developed and used to explain the roles of various incoming and outgoing reaction pathways and their influence on the overall catalytic behavior at electrode potentials ranging from U = 0.0 V to U = 1.2 V.

1.7 Formic Acid Oxidation on Pt(111)

1.7.1 Introduction to Formic Acid Oxidation

For our second and final example we present modeling of a second major fundamental reaction in electrochemistry: formic acid oxidation. Once again, DFT provides the foundation, but a two-dimensionally infinite Pt(111) slab model is used in place of the Pt₃₅ cluster used to study the ORR. The role of solvation effects is considered, however, an explicit solvation model is used. A kinetic rates model is extracted from DFT-characterized reaction pathways, and an electrode potential picture of the formic acid oxidation is compared to the experimental cyclic voltammogram (CV).

The electro-oxidation of formic acid (HCOOH) on Pt(111) and analogous transition metals has been the topic of numerous studies [65,108–137] due both to its fundamental role in electrochemistry and its importance for low-temperature fuel cell technologies. It has been studied under both gas phase (UHV) surface science and electrochemical (solvated) conditions. Gas phase HCOOH oxidation has been well characterized in surface science experiments [115–118], which reveal a single decomposition path which proceeds through a formate intermediate.

In contrast, there has been difficulty in characterizing the electrochemical oxidation of HCOOH experimentally; however, a dual-path mechanism, in which both so-called direct and indirect paths are utilized, is generally accepted [120–129]. The indirect pathway proceeds through a CO intermediate, a poisoning species which has been identified using *in situ* infrared reflection-adsorption spectroscopy (IRAS) [132,133]. In contrast, the reactive intermediate along the direct pathway is still being disputed, with some arguing for COH or CHO [134], some for COOH [119–120], others for HCOO [129–131], and still others for HCOOH [126–128]. Thus, as seen in Figure 1.27, there are at least three pathways to consider: the indirect pathway via CO, the direct pathway which begins with C—H activation, and a formate pathway (a second possibility within the direct path) which begins with O—H activation and thus proceeds via a formate intermediate.



Figure 1.27 Schematic representation of the proposed mechanisms for the oxidation of electrochemical HCOOH.

1.7.2

Density Functional Theory Calculations

The direct and formate pathways, which make up the so-called direct path, have been the topic of recent theoretical studies [135–137] aimed at nailing down the relevant reaction intermediate(s) for the direct path. In this example we present modeling strategies used to characterize these reaction pathways and point to how the mechanistic insights thus obtained can be used to explain CV measurements.

The DFT calculations presented here were performed using PBE, a generalized, gradient approximation (GGA) exchange-correlation functional proposed by Perdew, Burke and Einzerhof [138], as implemented in the CASTEP code [111]. Vanderbilt-type, ultrasoft pseudopotentials [139] were used to describe the nuclei and core electrons, while band states occupied by valence electrons were described using plane-waves with an energy cut-off of 400 eV. The Pt electrode was modeled as a five layer, $p(3 \times 3)$ Pt(111) slab, allowing adsorbate coverages as low as 1/9 ML. A vacuum region of >13 Å was left to separate neighboring slabs in the supercell geometry. For the numerical integration in reciprocal space required for periodic systems a 2 × 2 Monkhorst-Pack k-grid was used following convergence tests. During geometry convergence the top three layers of the Pt(111) slab were allowed to relax, while the bottom two layers were fixed at their bulk positions. A transition state search procedure employing linear and quadratic synchronous transit (LST/ QST) algorithms in conjunction with conjugate gradient methods was employed to locate transition states using CASTEP.

1.7.3

Gas Phase Reactions

In thoroughly investigating HCOOH oxidation on Pt(111) a variety of surface coverages and compositions as well as all reasonable, possible reaction pathways need to be considered. This has indeed been done [135–137]. Here, for the sake of



Figure 1.28 Reaction mechanisms for HCOOH oxidation without water. Here the potential profile at $\Theta_{\text{HCOOH}} = 1/9$ ML is illustrated.

illustration, we focus on two reaction pathways at low coverage (1/9 ML). Both reaction pathways begin with adsorbed HCOOH and end with CO_2 and two H adatoms. In the direct pathway, the C—H bond is cleaved first, resulting in a COOH intermediate which is further dehydrogenated (O—H bond dissociation) to form the final products (CO_2 and 2 H). In the formate pathway the O—H bond dissociates first to form a bi-dentate formate (HCOO_B) intermediate (both O atoms are bonded to the surface). One of the surface-O bonds then dissociates forming mono-dentate formate (HCOO_M), which then dissociates to yield CO_2 and H.

The energetics for these two pathways, based on DFT calculations are shown in Figure 1.28. The critical barrier for the direct pathway is the 1.83 eV needed to cleave the C—H bond in the first step. The two dehydrogenation barriers within the formate pathway are both less than 1 eV, making conversion of HCOO_B into HCOO_M, with a barrier of 1.27 eV, the rate-determining step. Thus under low-coverage, high vacuum (i.e., surface science) conditions, we anticipate that the formate pathway is preferred. Indeed, on the basis of vibrational frequencies obtained in experimental UHV measurements, it has been proposed that a HCOO species is the active intermediate [117].

1.7.4 Explicit Solvation Model

In Section 1.6.6 we illustrated the use of an implicit solvation model to account for electrostatic interactions between the solvent and solvated reaction molecules in the ORR. Here, we illustrate the use of an explicit solvent model in which explicit, solvating water molecules are introduced into the model to account for hydrogen bonding between the reaction molecules and water molecules which are part of the

electrochemical environment. In order to determine an appropriate number of water molecules to use in the explicit solvation model, along with their optimal locations and orientations, various configurations involving one, two and four water molecules per $p(3 \times 3)$ super cell were explored. Because solvating molecules are free to move around in an experiment, we anticipate that the lowest energy structure (for a given number of water molecules) is the most likely experimental structure for the number of water molecules. Similarly, among various possible solvation structures at a transition state, the most stable (i.e., the lowest energy) structure provides the barrier which is most relevant to the reaction rate. Among the solvation models tested, a water bilayer model consisting of four water molecules in an ice-like bilaver structure on the surface with HCOOH incorporated into the thus formed water network was found to be the most appropriate model using the critera discussed above and thus adopted [136]. The energy landscape for the direct and formate pathways using a water bilayer solvation model are presented in Figure 1.29. The most obvious effect of the solvating water molecules is the stabilization of H by formation of H₃O following O-H dissociation. This not only increases the overall exothermicity of the reaction from $\Delta E = -0.29$ eV to $\Delta E = -0.58$ eV, but reduces the O—H dissociation barrier by more than 50% from 0.94 to 0.29 eV and from 1.15 to 0.48 eV in the formate and direct pathways, respectively. The stabilizing influences of the hydrogen bonding within the water network also result in significant reductions to the barrier of the C-H dissociation step in the direct pathway (1.83 to 0.79 eV), and in the HCOO_B to HCOO_M transformation in the formate pathway (1.27 to 0.61 eV). In contrast, the C—H dissociation barrier in the formate pathway is only modestly reduced (0.71 to 0.58 eV). The net result is that the effective barriers for both pathways are considerably lower (i.e., the highest barriers for the formate



Reaction coordinate

Figure 1.29 Potential energy diagram comparing the two lowest reaction pathways of the Langmuir–Hinshelwood HCOOH oxidation reaction mechanisms using the water bilayer solvation model.

1.7 Formic Acid Oxidation on Pt(111) 63

HCOOH oxidation - direct pathway

$$HCOOH + 4 H_{2}O \xrightarrow{-0.33}{+0.79} COO + H + H_{3}O + 3 H_{2}O \xrightarrow{+1.01} COO + 4 H_{2}O \xrightarrow{-0.20}{+0.38} CO_{2} + 4 H_{2}O$$

$$HCOOH \text{ oxidation - formate pathway}$$

$$HCOOH + 4 H_{2}O \xrightarrow{-0.31}{+0.29} HCOO_{B} + H_{3}O + 3 H_{2}O \xrightarrow{+0.72}{+0.30} HCOO_{B} + 4 H_{2}O \xrightarrow{+0.34}{+0.68} HCOO_{M} + 4 H_{2}O$$

$$\xrightarrow{-0.68}{+0.73} CO_{2} + H_{3}O + 3 H_{2}O \xrightarrow{+0.41}{+0.30} CO_{2} + 4 H_{2}O$$

$$\xrightarrow{-0.68}{+0.73} CO_{2} + H_{3}O + 3 H_{2}O \xrightarrow{+0.41}{+0.30} CO_{2} + 4 H_{2}O$$

$$\xrightarrow{-0.68}{+0.73} CO_{2} + H_{3}O + 3 H_{2}O \xrightarrow{+0.41}{+0.41} CO_{2} + 4 H_{2}O$$

$$\xrightarrow{-0.68}{+0.73} CO_{2} + H_{3}O + 3 H_{2}O \xrightarrow{+0.41}{+0.30} U < 0.41$$

$$\xrightarrow{-0.68}{+0.73} CO_{2} + H_{3}O + 3 H_{2}O \xrightarrow{+0.41}{+0.30} U < 0.41$$

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$$\xrightarrow{-0.68}{+0.73} CO_{2} + H_{3}O + 3 H_{2}O \xrightarrow{+0.41}{+0.30} U < 0.41$$

$$\xrightarrow{-0.68}{+0.73} CO_{2} + H_{3}O + 3 H_{2}O \xrightarrow{+0.41}{+0.30} U < 0.41$$

$$\xrightarrow{-0.68}{+0.73} CO_{2} + H_{3}O + 3 H_{2}O \xrightarrow{+0.41}{+0.41} CO_{2} + 4 H_{2}O$$

$$\xrightarrow{-0.68}{+0.73} CO_{2} + H_{3}O + 3 H_{2}O \xrightarrow{+0.41}{+0.30} U < 0.41$$

processes considered in kinetic rates analysis. Reaction energies (italics) and barriers (bold) are given in eV above and below the reaction arrows. The electrode-potential dependence for

the reaction energies and barriers of CPET processes are given by including the appropriate correction as a function of U in the energy expression.

and direct pathways are reduced from 1.27 to 0.61 eV and from 1.83 to 0.79 eV, respectively), in the presence of the water bilayer. Nevertheless, the preference for the formate pathway over the direct pathway remains unchanged, as is evident in Figure 1.30.

1.7.5 Eley–Rideal Mechanisms and the Electrode Potential

Thus far we have only considered dehydrogenation processes resulting in neutral H or hydronium adsorbates. These are so-called LH-type reactions whose energetic landscapes have no direct dependence on the electrode potential. Alternatively we might consider ER-type reactions in which the dissociating H atom gives up its electron to the electrode surface and is dissolved into the electrolyte as a solvated proton. When we further consider that this proton is in equilibrium with solvated protons at the counter electrode, which are involved in hydrogen evolution (and is indeed free to migrate and participate in this reaction itself), then we can view the whole as a coupled protonelectron-transfer (CPET) process: If we note that the standard states

$$H^+_{(aq)} + e^- {\longrightarrow} \frac{1}{2} H_{2(g)}$$

of $H^+_{(aq)}$ and $H_{2(g)}$ are at equilibrium at the hydrogen reference electrode (HRE), then we can calculate the energy of a solvated proton as a function of electrode potential and pH as follows:

$$E_{\mathrm{H}_{(\mathrm{aq})}^{+}} = \frac{1}{2} E_{\mathrm{H}_{2(\mathrm{g})}} - \mathrm{pH} \cdot k_{\mathrm{B}} T \ln (10) - U = \frac{1}{2} E_{\mathrm{H}_{2(\mathrm{g})}} - k_{\mathrm{B}} T \ln \left(\left[H_{\mathrm{aq}}^{+} \right] \right) - U \quad (1.70)$$

Now that the electrode potential dependence of the reaction energy of a CPET process has been determined, a means for determining the barrier of a CPET process is needed. A CPET process consists of a series of proton transfers between water molecules which shuttle the proton from one electrode to the other. This

barrier has been estimated to be 0.3 eV based on coupled cluster singlet doublet (CCSD) calculations [86]. The reaction barrier is then assumed to be 0.3 eV above the energetically higher endpoint (i.e., product or reactant state). Thus, in the uphill direction the reaction has a barrier which is 0.3 eV higher than the reaction energy, and the downhill direction a barrier of 0.3 eV.

To model ER-type reaction pathways we need to introduce ER-type reaction steps, which remove the activated H atoms by transferring them as protons into the electrolytic phase, after they have dissociated from HCOOH. The energetics for these CPET steps can then be computed as explained above. The energetic land-scapes for the resulting ER-type pathways at 0 V and 1.0 V are shown in Figure 1.31a and b respectively. Along the direct pathway both CPET steps occur at the same stage of the pathway and can thus be combined into a single effective barrier. At zero



Figure 1.31 Comparison of Eley–Rideal HCOOH oxidation reaction mechanisms with the water bilayer solvation model (a) U = 0.0 V and (b) U = 1.00 V vs. RHE.

potential this barrier is large, as the reaction step is uphill, and is rate limiting. At U = 1.0 V the CPET steps are now downhill, so that the associated barrier is only 0.3 eV. Thus a different, potential-independent barrier (i.e., the barrier for the initial double deprotonation step) is rate limiting. In the case of the formate pathway, the added CPET steps take place immediately after each of the deprotonation steps. At zero potential the first of these has the largest barrier and is rate determining. However, since CPET steps accelerate as the potential increases, a potential-independent step (C—H bond dissociation) is rate limiting at 1.0 V. In the end the rate-limiting barrier for the direct pathway is always higher than that of the formate pathway, so that the formate pathway is always preferred.

1.7.6

Kinetic Rate Model of Formic Acid Oxidation

Finally, the DFT results for the energetics of the different competing reaction pathways were combined into a kinetic rate model using the method explained in Section 1.3.3.3. The role of co-adsorbed CO^{*} and OH^{*} was also considered [137]. From all of these possible pathways, the rate for the fastest pathway at the appropriate CO^{*} and OH^{*} coverage for electrode potentials between 0.0 and 1.2 V was considered to be a good approximation of the overall reaction rate. This potential-dependent rate is plotted in Figure 1.32 in conjunction with the experimental CV [118].

At low potentials (0.0 V < U < 0.4 V) the formate pathway, limited by a potentialdependent CPET process, is the dominant mechanism. This is corroborated by the experimental observation of HCOO_B at low potentials [127–131, 140]. Near 0.4 V the



Figure 1.32 Comparison of the experimental CV [118] (taken at a potential sweep rate of 50 mV s^{-1}) and the calculated potential-dependent rate constants.

potential-independent formate pathway becomes dominant and is the primary pathway going into the so-called negative differential resistance (NDR) region. Around 0.6 V the surface concentration of CO* increases dramatically and succeeds in tying up OH and thus disabling the direct pathway. This probably explains in part the low reactivity of the NDR region. The region of peak activity (0.85 V < U < 0.95) follows. Here the direct pathway, whose reactivity is enhanced by the presence of co-adsorbed CO* and OH*, dominates the reaction mechanism. Further increasing the electrode potential leads to the oxidative removal of CO*, which suppresses the direct pathway and leaves the formate pathway as the primary mechanism above 0.95 V [137].

1.7.7

Summary

The study of HCOOH electro-oxidation on Pt(111) presented in this section has given the opportunity to show the use of slab and explicit solvent models in DFT calculations. The resulting solvent network plays a crucial role in (de)stabilizing important reaction steps, and the use of experimental results to determine the appropriate solvent model (i.e., OH* and CO* coverages) for various electrode potentials illustrates an important strategy in developing simulation models: that is, taking advantage of experiment hints. While it would have been possible to derive these coverages entirely from theory, it was more efficient to take advantage of experimental results already in place, and thus avoid additional errors the theoretical derivation might have introduced. The qualitative comparison between the theoretically derived rate constants and the experimental CV, as well as rough comparisons involving other points of contact between theory and experiment (e.g., the experimental observation of COOH_B at low potentials as corroboration of the theoretically predicted mechanism) are typical examples of what must be done to compare results from theory and experiment and combine them to reach conclusions consistent with both.

1.8 Concluding Remarks

In this chapter much attention has been given to electronic structure theory and in particular to DFT. This is appropriate as these methods provide us with the most fundamental models of electrochemical systems (or parts thereof) available to us today, and because other levels within a multiscale modeling framework are typically built on this foundation of applied quantum mechanics. Furthermore, DFT has become a common tool in electrochemistry, such that the treatment of simple electrochemical systems is now a fairly routine application of DFT. The results of such DFT simulations can be readily and regularly translated into the language of experimental observables without the aid of intermediate models. Thus, DFT has often been able to stand on its own as a modeling tool in electrochemistry.

Nevertheless, there are many phenomena, which are not so easily described using only DFT models. One of these is growth processes, where the long-range structure and/or the order of events can be vital to the characterization of the overall process. Thus, kMC methods are a popular means of combining the individual adsorption and diffusion events, which can be modeled individually using DFT, into a coherent model of the entire growth process. Another example is the electrochemical double layer, a description of which requires the analysis of many more structures than routine applications of DFT are capable of tackling. Thus, molecular force fields are an ideal middleman *en route* from DFT to an experimentally meaningful description of the electrochemical double layer. While the quantitative capabilities of DFT increase, in terms of the number of atoms and geometries for which energies and densities can be routinely calculated, the size and complexity of the systems of interest to many electrochemists are increasing as well. At the same time the incentive for leveraging DFT's power by magnifying its results by placing it at the bottom of a multiscale modeling framework only increases as DFT calculations become more reliable and routine. Multiscale modeling in electrochemistry is still in its early stages and has a bright future ahead.

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