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Advances in Quantum Chemistry for Heterogeneous Catalysis

by

Richard Kang

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Martin Head-Gordon, Chair

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Spring 2026

Advances in Quantum Chemistry for Heterogeneous Catalysis

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Richard Kang

Abstract

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Professor Martin Head-Gordon, Chair

Heterogeneous catalysis is a highly important research area in chemistry that can address the climate crisis. Advances in computational chemistry tools, particularly those based on density functional theory (DFT), have been employed to uncover the underlying physics of the operation of catalysts and have contributed to their more efficient design. In this dissertation, we develop and apply computational schemes using density functional theory (DFT) to a broad range of topics relevant to heterogeneous catalysis. In the first half of the dissertation, we combine orbital-optimized (OO) single-reference methods with the one-electron exact two-component (X2C) Hamiltonian to model the ionization of core-electrons. In Chapter 2, we present a non-orthogonal, quasi-degenerate perturbation theory (NO-QDPT) approach for treating the spin-orbit coupling of core-electrons. This scheme is applied to a broad range of ionizations across the periodic table in order to assess its performance and identify its limits. The NO-QDPT approach demonstrates near-quantitative agreement with experimental core-electron binding energies for third-row elements, though its accuracy decreases for later first-row transition metals. In the second half of the dissertation, elementary ion-transfer reactions are modeled via Constant Electrode Potential (CEP) calculations. In Chapter 3, the adiabatic, reversible electrodedissolution of anodically polarized silver is modeled. By employing a hybrid implicit-explicit solvation model and the CEP protocol, the study successfully predicts reaction trajectories and free energy barriers that align with temperature-dependent experimental data. The findings reveal that the reaction barrier is a delicate competition between solvation, metal-metal bonding, and image charges. In Chapter 4, the role of hydroxide-mediated intermediates in cathodic copper degradation during the carbon dioxide reduction reaction (CO₂RR) is studied. CEP calculations show that hydroxide-mediated dissolution of exposed surface Cu atoms is potentially viable. Specifically, the formation and subsequent dissolution of [Cu(OH)₂]⁻ from surface defects is found to be energetically accessible and is facilitated by the formation of an image quadrupole. Together, these findings demonstrate that refined computational treatments of the electrode surface can provide a fundamental understanding of the surface chemistry governing the durability of heterogeneous systems.

To My Family.

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Chapter 1

Introduction

Heterogeneous catalysis involves two different phases of materials and aims to use the interface of the two to facilitate reactions that are difficult otherwise. [1–3] One of the most commonly utilized interfaces is the metal-to-solution interface, where external driving forces such as light or potential are applied to promote reactivity. Heterogeneous catalysis has a long history in chemistry and chemical engineering, but the 21st century has seen a significant shift towards sustainable chemical synthesis. Current research is heavily focused on the production of chemicals like multi-carbon products (e.g., alcohol, ethylene) and nitrogen-based chemicals (e.g., fertilizers) using industrial feedstock or direct air-capture. [4–6] Critical research areas such as carbon capture, energy storage, and renewable energy conversion also rely profoundly on heterogeneous catalysis for both generating and storing chemical energy. Given the significant threat of climate change posed by anthropogenic carbon dioxide emissions [7–9] heterogeneous catalysis stands as a powerful tool for mitigating climate change by closing the anthropogenic carbon-, hydrogen-, and nitrogen-cycles.

Developments in computational and theoretical chemistry have allowed a change in paradigm for catalyst design. Historically, catalyst development relied on a slow trial-and-error approach. A famous early example is the development of the Haber–Bosch process for the production of ammonia in the early 1900s. [1, 2, 10] This, however, changed in the late 20th century as computational methods became increasingly reliable and cost-effective. Today, it is unambiguously clear that a multitude of heterogeneous catalysts can be simulated and screened through computational protocols, yielding more efficient platforms for catalysis. Density functional theory (DFT) calculations, in particular, is now frequently applied in innumerable studies to uncover elementary reactions and intermediates that govern complex mechanisms. [11–16] The routine use of DFT has also stimulated further theoretical development of methods such as inclusion of potential and efficient algorithms to search different chemical conformations. [11, 17–20]

In this dissertation, we are interested in the application and development of quantum chemistry methods for studying the fundamental physical chemistry that govern various aspects of heterogeneous catalysis. This work will cover a broad range of topics, from core-ionization of metals to ion-transfer reactions at the electrode. We first review the basic principles of molecular quantum chemistry, which lays the foundation for modern density functional theory. Our discussion in this chapter will largely be limited to non-relativistic, time-independent framework, although its

extension to relativistic realm will be introduced briefly.

Throughout this dissertation, we employ atomic units to set the mass of electron (m_e), the elementary charge (e), Bohr's Radius (a_0), and reduced Planck's constant ($\hbar$) as unity: i.e., $m_e = e = a_0 = \hbar = 1$. All bold quantities (i.e., $\mathbf{A}$) represent operators whose matrix elements can be evaluated within a suitable basis. All vector quantities are noted with an arrow above (i.e., $\vec{A}$).

1.1 Non-relativistic Quantum Chemistry

In quantum mechanics, one is interested in solving the *time-dependent Schrödinger Equation* (TDSE)

$$\mathbf{H}(t) |\Psi(t)\rangle = i \frac{\partial}{\partial t} |\Psi(t)\rangle \quad (1.1)$$

The Hamiltonian $\mathbf{H}$ of the system governs the quantum mechanics. The corresponding state $|\Psi(t)\rangle$ contains all the information about how the system changes over time. If $\mathbf{H}(t)$ does not depend on time, one can separate t out of the equation to arrive at the *time-independent Schrödinger Equation* (TISE)

$$\mathbf{H} |\Psi_i\rangle = E_i |\Psi_i\rangle \quad (1.2)$$

Solving Eq. (1.2) yields the set of *stationary states* $\{|\psi_i\rangle\}$ which form a complete basis. That is, any arbitrary state of the system can be described by a linear combination of $|\psi_i\rangle$. The projection of eigenstate $\{|\psi_i\rangle\}$ onto a certain variable (e.g. position $\vec{r}$ or momentum $\vec{k}$) yields the *wavefunction* $\Psi(\vec{r}) = \langle \vec{r} | \Psi \rangle$.

In quantum chemistry, we are interested in solving the TISE for any molecular Hamiltonian $\mathcal{H}$ of the system composed of N electrons and M nuclei. In the non-relativistic limit and in the absence of any external fields/perturbations, $\mathcal{H}$ includes five terms: kinetic energy of the electrons ($\mathbf{T}_e$), kinetic energy of the nuclei ($\mathbf{T}_n$), nuclear-electron attraction ($\mathbf{V}_{ne}$), electron-electron repulsion ($\mathbf{V}_{ee}$), and nuclear-nuclear repulsion ($\mathbf{V}_{nn}$)

$$\mathcal{H} = \mathbf{T}_e + \mathbf{T}_n + \mathbf{V}_{ne} + \mathbf{V}_{ee} + \mathbf{V}_{nn} \quad (1.3)$$

The kinetic energy terms are

$$\mathbf{T}_e = - \sum_{i=1}^N \frac{1}{2} \vec{\nabla}_i^2 \quad (1.4)$$

$$\mathbf{T}_n = - \sum_{A=1}^M \frac{1}{2M_A} \vec{\nabla}_A^2 \quad (1.5)$$

The indices $\{i, j, \dots\}$ denote electrons and the indices $\{A, B, \dots\}$ denote nuclei. $\{M_A\}$ are the masses of the nuclei in atomic units. Likewise, the potential energy terms $\mathbf{V}_{ne}$, $\mathbf{V}_{nn}$, and $\mathbf{V}_{ee}$ are

$$\mathbf{V}_{ne} = - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} \quad (1.6)$$

$$\mathbf{V}_{nn} = \frac{1}{2} \sum_{A \neq B}^M \frac{Z_A Z_B}{|\vec{R}_A - \vec{R}_B|} \quad (1.7)$$

$$\mathbf{V}_{ee} = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (1.8)$$

$\{\vec{R}_A\}$ and $\{\vec{r}_i\}$ are the positions of the nuclei and electrons in three-dimensional space, respectively. Z_A and Z_B are the nuclear charges of the atoms A, B .

The simple form of Eq. (1.3) belies the complexity of actually solving Eq. (1.2). In fact, obtaining analytical solutions for $\mathcal{H}$ — finding its corresponding eigenstates and energies — has remained virtually impossible beyond Hydrogen-like atoms. In addition, the wavefunction of this Hamiltonian depends on both $3M$ nuclear degrees of freedom and as $3N$ electronic degrees of freedom. Therefore, if we wish to make any further progress, we must apply a suitable set of approximations, tailored to the nature of the problem under consideration.

1.1.1 The Born-Oppenheimer Approximation

Recall that the proton-to-electron mass ratio is ~ 1836 . [21] While this figure is already large, most nuclei have more than one proton (as well as neutrons). Nuclei are therefore significantly much heavier than the electrons and consequently move on a much slower timescale. This leads us to the first and the most important approximation in quantum chemistry: the *Born-Oppenheimer* (BO) approximation. Under the BO approximation, one treats the motion of electrons in a stationary field of nuclei whose positions are fixed. [22–24] Within the BO approximation, one can write the *electronic Hamiltonian* $\mathcal{H}_e$ that describes the motion of the electrons in this clamped nuclei field

$$\mathcal{H}_e = \mathbf{T}_e + \mathbf{V}_{ne}(\vec{R}) + \mathbf{V}_{ee} + V_{nn}(\vec{R}) \quad (1.9)$$

Note that the nuclear-nuclear repulsion term is no longer an operator but a *scalar* quantity (i.e., V_{nn} and not $\mathbf{V}_{nn}$) because of the fixed positions of the nuclei. The nuclear kinetic energy term $\mathbf{T}_n$ is also removed. The BO approximation also allows us to decouple the nuclear and electronic degrees of freedom. The stationary state $|\Psi\rangle$ of the total molecular Hamiltonian $\mathcal{H}$ can therefore be approximated as a BO product

$$|\Psi\rangle \approx |\Psi_{\text{BO}}\rangle = |\Phi_n\rangle \otimes |\Theta_m\rangle \quad (1.10)$$

where $|\Phi_n\rangle$ is the electronic eigenstate of $\mathcal{H}_e$, and $|\Theta_m\rangle$ is the nuclear eigenstate. The electronic eigenfunction Φ_n is now parametrically dependent on the nuclear position such that the total BO

product wavefunction is written as

$$\Psi_{\text{BO}}(\vec{r}, \vec{R}) = \Phi_n(\vec{r}; \vec{R}) \Theta_n(\vec{R}) \quad (1.11)$$

Under the BO approximation, the task of finding the stationary states of $\mathcal{H}$ is reduced to finding those of $\mathcal{H}_e$ and then subsequently solving for the total $\mathcal{H}$. This leads to a simplified picture where nuclear configurations are described by a hyper-dimensional *potential energy surface* $E(\{\vec{R}\})$ (PES) determined by eigenvalues of $\mathcal{H}_e$ for a fixed $\vec{R}$. While the BO approximation does hold for many cases, there are cases where its breakdown is important such as non-adiabatic chemical dynamics that involve multiple electronic states and transitions between them. Though this topic is out of the scope of this dissertation, we direct interested readers to Refs [25–29].

1.1.2 Orbitals and Slater Determinants

Unfortunately, the BO approximation alone is not sufficient. The origin of the remaining complexity stems from $\mathbf{V}_{ee}$, a two-body operator depending on all possible pairs of electrons, which prevents separation of variables and obtaining analytical solutions. It is therefore attractive to start from systems without $\mathbf{V}_{ee}$: *hydrogen-like atoms*. The Hamiltonian for such systems is

$$\mathcal{H}_e^{\text{H-like}} = \mathbf{T}_e + \mathbf{V}_{ne} = -\frac{1}{2}\nabla^2 - \frac{Z_A}{r} \quad (1.12)$$

Fortunately enough, the analytical solutions to hydrogen-like atoms are available. The exact expressions for the wavefunctions of hydrogen-like atoms are tabulated in introductory quantum mechanics textbooks. [30–32] They can be written in the following form

$$\psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) Y_l^m(\theta, \phi). \quad (1.13)$$

The radial part $R_{n,l}(r)$ of $\psi_{n,l,m}$ is characterized by quantum numbers n, l and is written in terms of the associated Laguerre polynomials. The angular part $Y_l^m(\theta, \phi)$ of $\psi_{n,l,m}$ is characterized by quantum numbers l, m and such functions are known as spherical harmonics. This characterization does break when spin-orbit coupling is strong, which will be discussed in-depth in Chapter 2 of this dissertation along with relativistic quantum chemistry.

Another necessary consideration is quantum mechanical *spin*. Elementary and composite particles carry an intrinsic angular momentum called *spin*. The spin eigenstates of the z -component spin operator $\mathbf{S}_z$ are

$$\mathbf{S}_z |\uparrow\rangle = \frac{1}{2} |\uparrow\rangle \quad (1.14)$$

$$\mathbf{S}_z |\downarrow\rangle = -\frac{1}{2} |\downarrow\rangle \quad (1.15)$$

$|\uparrow\rangle$ and $|\downarrow\rangle$ are also commonly represented as $|0\rangle$ and $|1\rangle$; or α and β . Here we adopt the last convention: α and β . We can then add the electron-spin degree of freedom to the spatial wavefunctions of the hydrogen-like atoms: i.e.,

$$\chi_1(\tau_1) \equiv \chi_1(\vec{r}_1, s_1) = \phi_1(\vec{r}) \sigma(s_1) \quad (1.16)$$

where s_1 is a spin-coordinate. χ_i are called *spin-orbitals*, and the spatial part ϕ_i (with $\sigma(s_1)$ integrated out) are called *spatial orbitals*. Each of these orbitals can represent each electron, and may be used as a starting point for obtaining the wavefunction for a multi-electron system.

What is the easiest way to write down a solution for a multi-electron system? One could simply form a product state of multiple spin-orbitals. Indeed, this is the *Hartree product* which describes a many-electron system as an independent product of one-particle spin-orbitals. [33] Unfortunately, the Hartree product violates an important spin-statistics rule. A multi-particle quantum mechanical wavefunction must obey particle exchange symmetry. This means that wavefunctions must remain the same (subject to a phase) under the particle exchange operator $\mathbf{P}_{12}$ that permutes the coordinates of two particles. This gives rise to two types of particles that are either *symmetric* or *antisymmetric* under exchange:

$$\mathbf{P}_{12}\Psi(\tau_1, \tau_2, \dots) = \Psi(\tau_2, \tau_1, \dots) \quad \text{symmetric.} \quad (1.17)$$

$$\mathbf{P}_{12}\Psi(\tau_1, \tau_2, \dots) = -\Psi(\tau_2, \tau_1, \dots) \quad \text{anti-symmetric.} \quad (1.18)$$

The particles that are symmetric under $\mathbf{P}_{12}$ are *bosons* and follow *Bose-Einstein statistics* (BE) [34]; the particles that are anti-symmetric under $\mathbf{P}_{12}$ are *fermions* and follow *Fermi-Dirac statistics* (FD). [35, 36] Electrons are fermions, and therefore their multi-electron wavefunction must be anti-symmetrized. The *Slater determinant* improves upon the simple Hartree product by satisfying this requirement [37, 38]

$$\Phi(\tau_1, \tau_2, \tau_3, \dots, \tau_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\tau_1) & \chi_2(\tau_1) & \dots & \chi_N(\tau_1) \\ \chi_1(\tau_2) & \chi_2(\tau_2) & \dots & \chi_N(\tau_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\tau_N) & \chi_2(\tau_N) & \dots & \chi_N(\tau_N) \end{vmatrix} \quad (1.19)$$

Let us consider how the mathematical properties of the determinant allow us to follow FD statistics:

- Property: The determinant changes sign upon interchanging 2 rows or columns.
Consequence: Exchanging two particles is equivalent to exchanging two columns (or rows) of the determinant. Therefore, a Slater determinant obeys the FD statistics.
- Property: The determinant vanishes if any two rows or columns are equal.
Consequence: Since two columns (or rows) of the determinant are same, two electrons occupy the same spin-orbital. This however makes the wavefunction be 0, which means that such state does not exist. This is the *Pauli Exclusion Principle*. [39]

So far, we made no assumptions about the single-particle orbitals, aside from their dependence on spatial and spin coordinates. The most general expression for a single-particle orbitals is a complex-valued linear combination of the $\mathbf{S}_z$ eigenstates α and β , with their respective spatial components $\{\phi^\alpha(\vec{r}), \phi^\beta(\vec{r})\}$

$$\chi_i(\vec{r}, s) = c_\alpha \phi_i^\alpha(\vec{r}_i) \alpha(s_i) + c_\beta \phi_i^\beta(\vec{r}_i) \beta(s_i) \quad (1.20)$$

Orbital Types	General Form	Symmetries
Generalized	$\chi_i(\vec{r}_i, s_i) = c_\alpha \phi_i^\alpha(\vec{r}_i) \alpha(s_i) + c_\beta \phi_i^\beta(\vec{r}_i) \beta(s_i)$	Complex ϕ_i (cG): None Real ϕ_i (G): $\mathbf{K}$
Unrestricted	$\chi_i(\vec{r}, s_i) = \phi_i^\alpha(\vec{r}_i) \alpha(s_i) \text{ or } \phi_i^\beta(\vec{r}_i) \beta(s_i)$ $\phi_i^\alpha \neq \phi_i^\beta$	Complex ϕ_i (cU): $\mathbf{S}_z$ Real ϕ_i (U): $\mathbf{K}, \mathbf{S}_z$
Restricted	$\chi_i(\vec{r}, s) = \phi_i(\vec{r}_i) \alpha(s_i) \text{ or } \phi_i(\vec{r}) \beta(s)$ i.e., $\phi_i^\alpha = \phi_i^\beta$ applied to U orbitals	Complex ϕ_i (cR): $\mathbf{S}^2, \mathbf{S}_z$, Real ϕ_i (R): $\mathbf{K}, \mathbf{S}^2, \mathbf{S}_z, \Theta$

Table 1.1: All possible orbital types and the corresponding symmetries each type preserves.

This defines the *complex-generalized* (cG) class of orbitals. Furthermore, if we restrict the spatial component to be real-valued, it reduces to real-generalized, or simply, *generalized* orbitals (G). We may then choose to apply various symmetry restrictions. First, let us require that all single-particle orbitals be an eigenstate of $\mathbf{S}_z$. This leads to the *unrestricted* orbitals (U)

$$\chi_i(\vec{r}_i, s) = \phi_i^\alpha(\vec{r}_i) \alpha(s_i) \quad \text{or} \quad \phi_i^\beta(\vec{r}_i) \beta(s_i) \quad (1.21)$$

Furthermore, let us require that α -type and β -type orbitals have identical spatial orbitals (i.e., preserve spatial symmetry). We then obtain the *restricted* orbitals (R)

$$\chi_i(\vec{r}_i, s_i) = \begin{cases} \phi_i(\vec{r}_i) \alpha(s_i) \\ \phi_i(\vec{r}_i) \beta(s_i) \end{cases} \quad (1.22)$$

Imposing restrictions on the choice of orbitals have consequences on the symmetries obeyed by the electronic wavefunction. The electronic Hamiltonian $\mathcal{H}_e$ commutes with several operators, such as the time-reversal Θ , complex conjugation $\mathbf{K}$, total spin $\mathbf{S}^2$ and the z-component spin-operator $\mathbf{S}_z$. The electronic wavefunction should therefore also be an eigenstate of all of these operators. For a trial Slater determinant, this is only true in the case of real restricted orbitals. A solution constructed using unrestricted orbitals is no longer an eigenfunction of $\mathbf{S}_z$. Lifting all constraints leads to a Slater determinant that does not obey any of the symmetries. Though one might find these violations troubling, these symmetry broken solutions nonetheless can be very useful approximations to the true wavefunction. Consider as an example the infamous failure of restricted orbitals in properly describing bond dissociation, and contrast that failure with the success of unrestricted orbitals for the same problem. [38] In addition, the determinant formed by unrestricted or generalized orbitals lowers energy than its restricted counterpart. Table 1.1 shows all possible types of orbitals with the corresponding symmetries each type preserves. We encourage readers to consult Refs [40–44] and their footnotes for further discussion on determinant stability and symmetry breaking.

1.1.3 The Hartree-Fock (HF) Theory

If we want to use a single Slater determinant $|\Phi\rangle$ composed of orbitals $\{\chi_i\}$ to represent a multi-electron wavefunction, the natural question that follows is how to find the best set of orbitals for $|\Phi\rangle$. We may use the variational principle to obtain such orbitals. Any trial wavefunction is bounded by the true, exact ground-state energy of the system per the *variational principle*:

$$E_{\text{exact}} \leq \frac{\langle \Psi_{\text{trial}} | \mathbf{H} | \Psi_{\text{trial}} \rangle}{\langle \Psi_{\text{trial}} | \Psi_{\text{trial}} \rangle} \quad (1.23)$$

Eq. (1.23) is true for any Hamiltonian governed by the TISE (Eq. (1.2)). Therefore, the best Slater determinant and its orbitals can be obtained by minimizing the expectation value of the Hamiltonian. Here we review a few important terms involved in evaluating $\langle \mathcal{H}_e \rangle$:

$$E_0 = \langle \Phi_0 | \mathcal{H}_e | \Phi_0 \rangle \quad (1.24)$$

$$= \langle \Phi_0 | \mathbf{T}_e | \Phi_0 \rangle + \langle \Phi_0 | \mathbf{V}_{ne} | \Phi_0 \rangle + \langle \Phi_0 | \mathbf{V}_{ee} | \Phi_0 \rangle + V_{nn} \quad (1.25)$$

$$\langle \Phi_0 | \mathbf{T}_e | \Phi_0 \rangle = -\frac{1}{2} \sum_i^N \int d\tau \chi_i^*(\tau) \nabla_{\vec{r}}^2 \chi_i(\tau) \quad (1.26)$$

$$\langle \Phi_0 | \mathbf{V}_{ne} | \Phi_0 \rangle = - \sum_i^N \sum_A^M \int d\tau \chi_i^*(\tau) \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} \chi_i(\tau) \quad (1.27)$$

Eq. (1.26) and (1.27) only sum over single orbitals of the bra and the ket, and thus are considered one-electron terms. The electron-electron repulsion term however depends on two electrons from both the bra and the ket:

$$\langle \Phi_0 | \mathbf{V}_{ee} | \Phi_0 \rangle = \frac{1}{2} \sum_{i \neq j} (J_{ij} - K_{ij}) \quad (1.28)$$

$$J_{ij} = \iint d\tau d\tau' \chi_i^*(\tau) \chi_j^*(\tau') \frac{1}{|\vec{r} - \vec{r}'|} \chi_i(\tau) \chi_j(\tau') \equiv \langle ij | ij \rangle \quad (1.29)$$

$$K_{ij} = \iint d\tau d\tau' \chi_i^*(\tau) \chi_j^*(\tau') \frac{1}{|\vec{r} - \vec{r}'|} \chi_j(\tau) \chi_i(\tau') \equiv \langle ij | ji \rangle \quad (1.30)$$

$J_{ij} = \langle ij | ij \rangle$ is the *coulomb* integral, the electrostatic repulsion between an electron in ϕ_i with the other in ϕ_j . $K_{ij} = \langle ij | ji \rangle$ is however a purely quantum mechanical term arising from the FD statistics and lacks a classical analogue. It prevents two electrons of the same spin from closely approaching each other, thus mitigating the mean-field repulsion J_{ij} . It is called the *exchange* integral, referring to the permutation of coordinates compared to J_{ij} term. Variational minimization of $\langle \mathcal{H}_e \rangle$ through changes in $\{\phi_i\}$ yields the *Hartree-Fock equation*, [33, 38, 45–48] which is an eigenvalue problem for each single-particle orbital that yields the best set of $\{\chi_i\}$

$$\mathbf{F}\chi_i(\tau_1) = \left[\mathbf{h}_{\text{core}} + \sum_j \mathbf{J}_j - \mathbf{K}_j \right] \chi_i(\tau_1) = \epsilon_i \chi_i(\tau_1) \quad (1.31)$$

where each operator is defined as

$$\mathbf{h}_{\text{core}} = -\frac{1}{2}\nabla^2 - \sum_A \frac{Z_A}{|\vec{R}_A - \vec{r}|} \quad (1.32)$$

$$\mathbf{J}_j \chi_i(\tau_1) = \left(\int d\tau_2 \frac{\chi_j^*(\tau_2) \chi_j(\tau_2)}{|\vec{r}_1 - \vec{r}_2|} \right) \chi_i(\tau_1) \quad (1.33)$$

$$\mathbf{K}_j \chi_i(\tau_1) = \left(\int d\tau_2 \frac{\chi_j^*(\tau_2) \chi_i(\tau_2)}{|\vec{r}_1 - \vec{r}_2|} \right) \chi_j(\tau_1) \quad (1.34)$$

This shows that HF is a mean-field theory where a single electron experiences the average field generated by the other electrons through $\mathbf{J}$ and $\mathbf{K}$. Although the problem has the appearance of an eigenvalue problem and its solution appears to be straightforward, the $\mathbf{J}$ and $\mathbf{K}$ terms are dependent on the $|\chi_i\rangle$, so the Hartree-Fock equations must be solved iteratively. The ϵ_i that appears in (1.31) originates as a Lagrange multiplier to enforce the orthonormality of the orbitals, but it may also be assigned physical meaning as it corresponds to the eigenvalue of each orbital and can be interpreted as the orbital energy [49].

1.1.4 Electron Correlation and Wavefunction Theories

HF theory neglects correlation between many different electrons. One simple way to understand this deficiency is to calculate the joint probability of finding two electrons at positions $\vec{r}$ and $\vec{r}'$ the He atom:

$$p(\vec{r}, \vec{r}') = \int ds ds' \Phi_{\text{He}}^*(\vec{r}, \vec{r}', s, s') \Phi_{\text{He}}(\vec{r}, \vec{r}', s, s') \quad (1.35)$$

$$= |\Phi_{\text{He}}(\vec{r}, \vec{r}')|^2 = |\phi_1(\vec{r}) \phi_2(\vec{r}')|^2 = |\phi_1(\vec{r})|^2 |\phi_2(\vec{r}')|^2 \quad (1.36)$$

Here, the probability of finding the second electron at some position $\vec{r}'$ is independent of the probability of finding the first electron at some position $\vec{r}$. In other words, there is no correlation between the two electrons. This is clearly unphysical, as two electrons will repel and disfavor a spatially close arrangement. The neglect of *electron correlation* is therefore a critical deficiency in Hartree-Fock theory.

Let us define the electron-correlation energy E_{corr} as the difference between the HF and the exact ground state energies

$$E_{\text{corr}} \equiv E_{\text{exact}} - E_{\text{HF}} \quad (1.37)$$

HF captures approximately 99% of the exact *absolute* ground state energy for most systems, so it is natural for one to ask how important E_{corr} is. Unfortunately, E_{corr} is highly important for chemical problems. Most of chemistry involves complex processes such as bond dissociation or electron transfer that may involve changes in spin states and electron numbers. Chemistry also involves relative energies, the difference of absolute energies between the initial and final states.

This requires a much finer scale of comparison. John Pople famously suggested 1 kcal/mol as a target accuracy in his Nobel Lecture (commonly referred to as “*chemical accuracy*”) [50] which is ~ 4 orders of magnitude smaller than the scale of atomic units of energy. There are numerous cases where the lack of electron correlation becomes a significant hurdle in describing chemical changes.

- HF cannot describe dispersion interaction between molecules: e.g., only through electron correlation do the noble gases liquefy.
- HF fails to predict bonding of F_2 molecule.
- HF significantly underestimates the bond energy of H_2 by 25%.

The inclusion of electron correlation is therefore critical for chemistry.

Describing electron correlation is in principle, straightforward. Following the linear variational principle, it is done by adding all possible Slater determinants into the ansatz

$$|\Psi\rangle = |\Phi_0\rangle + \sum_i^a t_i^a |\Phi_i^a\rangle + \sum_{i \neq j}^{a \neq b} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots \quad (1.38)$$

where the indices i, j refer to occupied orbitals and the indices a, b refer to virtual (unoccupied) orbitals. Each substituted determinant $|\Phi_{i,\dots}^{a,\dots}\rangle$ represents removing one or more electrons from the occupied orbitals $i, \dots$ and populating one or more virtual orbitals $a, \dots$. The $\{t_i^a, t_{ij}^{ab}, \dots\}$ are amplitudes corresponding to such determinant. This protocol is described as full configuration interaction (FCI) in the literature, as each Slater determinant corresponds to a different electronic configuration. FCI however has a computational cost that scales exponentially with system size, and is computationally intractable even on modern supercomputers for all but the smallest of systems. In fact, it was only in 2025 that the first near numerically exact, FCI-level calculation using more than a trillion determinants on a triatomic system was reported. [51] Therefore, our further discussion of the correlated wavefunction theories focus on discovering the effective approximations to the FCI wavefunction.

If a single-determinant $|\Phi_0\rangle$ has the dominant character of the ground state, we may simply start from $|\Phi_0\rangle$ and build up the remaining contribution as small additions. Such systems are often characterized as demonstrating *dynamic* or *weak* correlation in the literature. A comprehensive presentation of correlated wavefunction theory can be found in textbooks such as Refs [48] and [52]. Here we highlight two methods that can treat dynamic correlation here

- Møller-Plesset perturbation theory [53, 54]: An approach that applies a perturbation theory on the difference between the Fock operator and $\mathcal{H}_e$. The second order Møller-Plesset perturbation theory (MP2) scales as the fifth power of the system size N (i.e. $O(N^5)$) and is the simplest correlated wavefunction method.
- Coupled cluster methods [55, 56]: Uses a truncated exponential ansatz for wavefunction and solves the system of equations obtained by projecting the ansatz onto the corresponding

subspace of excitations. Simplest is the coupled cluster singles and doubles (CCSD), which scales as $O(N^6)$.

Both MP2 and CCSD demonstrate significant improvement of HF, but do not generally achieve the chemical accuracy. [57] The latter is only achieved by perturbative inclusion of triples into CCSD, known as CCSD(T), which is often called the “gold-standard.” [58, 59]

Some systems involve electrons experiencing intense inter-electron correlation relative to their kinetic and attractive energies which result in favoring unpaired configurations. In such cases, a single Slater determinant may be inadequate for the proper representation of a ground state, and solving HF equations may break the spatial symmetry of the orbitals in an attempt to approximate such inter-electron correlation. The resulting solution often demonstrates high spin-contamination, a significant deviation from the expected value of $\langle S^2 \rangle$. [44] These systems are said to exhibit *static* or *strong* correlation in the literature. One hand-tuned approach for strong correlation is to use more than one reference determinants and perform FCI within a specifically designated “active space”, a subset of orbitals defined by the user. One may also employ correlated wavefunction theory approaches using the determinants generated within active space. Such methods are often called “multireference” electronic structure methods. We direct interested readers to review Refs. [48, 60–64] and references therein for a detailed presentation.

1.2 Density Functional Theory

So far, we focused on obtaining the solutions to the electronic Hamiltonian $\mathcal{H}_e$ via an approximate multi-electron wavefunction. The clear disadvantage of this approach is the computational scaling. Each electron of $\mathcal{H}_e$ must be described by 3 spatial coordinates: An N -electron system therefore requires $3N$ spatial degrees of freedom. Let us assume that we want to model CO adsorption on a small cluster of 8 Cu atoms, which has $6+8+8\times 29 = 246$ electrons. While one may rightfully argue that this model system is too small to represent a catalytic system, it already requires $3^{246} \approx 10^{118}$ spatial degrees of freedom, a number that is larger than the total number of atoms in this universe!

Fortunately, density functional theory (DFT) takes a vastly different approach to this problem by focusing on the electronic density of the system $\rho(\vec{r})$. DFT has enjoyed extensive research and development since the beginning of its application to chemistry in the mid-twentieth century [65] and has undeniably been the workhorse of modern computational catalysis studies. It continues to be important in emerging data-driven and machine-learning (ML) atomistic models as it provides the benchmark data for describing ground state energies. [66–68] In this section, we give a brief overview of the theoretical background that underpins (Kohn-Sham) DFT, as well as a summary of the functionals currently available to practitioners of DFT.

1.2.1 The Hohenberg-Kohn Theorems

The two Hohenberg-Kohn theorems lay the theoretical footing for density functional theory. We summarize their proofs and results below. [69]

The First Hohenberg-Kohn (HK) Theorem. The first HK theorem states that for any system of interacting particles, the ground state density $\rho_0(\vec{r})$ is uniquely determined by the corresponding external potential $V_{\text{ext}}(\vec{r})$. For our case, v_{ext} is the nuclei-electron attraction term.

We prove this theorem by contradiction. Suppose that two different external potentials $V_1(\vec{r})$ and $V_2(\vec{r})$ both lead to $\rho_0(\vec{r})$. Then, both $\rho_0(\vec{r})$ must have two different corresponding ground state wavefunctions $|\Psi_1\rangle$ and $|\Psi_2\rangle$. This leads to following two different equations

$$(\mathbf{H}_u + V_1) |\Psi_1\rangle = E_1 |\Psi_1\rangle \quad (1.39)$$

$$(\mathbf{H}_u + V_2) |\Psi_2\rangle = E_2 |\Psi_2\rangle \quad (1.40)$$

where $\mathbf{H}_u$ contains the internal terms (for chemistry, these are the electron kinetic energy and electron-electron repulsion). Per the variational principle (Eq. (1.23)), the $\langle \Psi_2 | \mathbf{H}_u + V_1 | \Psi_2 \rangle$ must be larger than E_1 . Thus

$$E_1 = \langle \Psi_1 | \mathbf{H}_u + V_1 | \Psi_1 \rangle < \langle \Psi_2 | \mathbf{H}_u + V_1 | \Psi_2 \rangle \quad (1.41)$$

$$\langle \Psi_1 | \mathbf{H}_u | \Psi_1 \rangle < \langle \Psi_2 | \mathbf{H}_u | \Psi_2 \rangle \quad (1.42)$$

But the opposite is also true

$$E_2 = \langle \Psi_2 | \mathbf{H}_u + V_2 | \Psi_2 \rangle < \langle \Psi_1 | \mathbf{H}_u + V_2 | \Psi_1 \rangle \quad (1.43)$$

$$\langle \Psi_2 | \mathbf{H}_u | \Psi_2 \rangle < \langle \Psi_1 | \mathbf{H}_u | \Psi_1 \rangle \quad (1.44)$$

Eqs. (1.42) and (1.44) contradict each other. Thus our assumption is invalid and the first HK theorem is proven. To summarize, the first Hohenberg-Kohn theorem shows that ρ_0 *alone* uniquely defines the V_{ext} .

The Second Hohenberg-Kohn (HK) Theorem. The first HK theorem shows that there exists a functional that maps the ground state density ρ_0 to the ground state energy E_0 and thus the true wavefunction $|\Psi_0\rangle$. We may write such a functional $E_0[\rho_0(\vec{r})]$ as

$$E_0[\rho_0(\vec{r})] = T[\rho_0(\vec{r})] + V_{ee}[\rho_0(\vec{r})] + \int d\vec{r} V_{\text{ext}}\rho_0(\vec{r}) \quad (1.45)$$

where $T[\rho_0(\vec{r})]$ is the kinetic energy functional, $V_{ee}[\rho_0(\vec{r})]$ is the electron-electron interaction functional, and the last integral is the classical electrostatic electron-nuclear attraction.

The second HK theorem states that the density ρ_0 that yields the global minimum of the functional represents the true ground state: i.e., $E_0[\rho_0(\vec{r})] \leq E_0[\rho'(\vec{r})]$. The proof is simple if we invoke the variational principle again. Based on HK theorem 1, we may set another trial density ρ' with a corresponding wavefunction Ψ' . By the variational principle

$$E_0 = E_0[\rho_0(\vec{r})] = \langle \Psi_0 | \mathbf{H}_u + V_{\text{ext}} | \Psi_0 \rangle \leq \langle \Psi' | \mathbf{H}_u + V_{\text{ext}} | \Psi' \rangle = E_0[\rho'(\vec{r})] \quad (1.46)$$

where $|\Psi_0\rangle$ is the corresponding wavefunction for the true ground state.

1.2.2 Levy's Constrained Search

Now that we have proven the existence of our functional, an important question arises: How will we find such a functional? The complexity arises from the fact that we must determine if a found density is v -representable (that is, ρ_0 originates from a proper electronic wavefunction and a valid external potential V_{ext}).

Levy proposed a different approach that utilizes a constrained minimization protocol which searches through sets of wavefunctions $\{\Psi\}$ comprised of N -fermions. [70] The protocol first performs search over all N -particle (i.e., N -representable) wavefunctions instead of ρ_0 by breaking the Hilbert space into sectors of $\{|\Psi_\rho\rangle\}$ where each produces identical densities ρ . Once an optimal subspace is found, then a search over that subspace to find that ρ which minimizes E_0 is performed:

$$E_0[\rho_0(\vec{r})] = \min_{\rho} \left\{ \min_{|\Psi\rangle \rightarrow \rho} \langle \Psi | \mathbf{H}_u + V_{\text{ext}} | \Psi \rangle \right\} \quad (1.47)$$

$$= \min_{\rho} \left\{ \min_{|\Psi\rangle \rightarrow \rho} \langle \Psi | \mathbf{H}_u | \Psi \rangle + \int d\vec{r} V_{\text{ext}} \rho_0(\vec{r}) \right\} \quad (1.48)$$

where

$$\mathcal{F}[\rho_0(\vec{r})] = \min_{|\Psi\rangle \rightarrow \rho} \langle \Psi | \mathbf{H}_u | \Psi \rangle = \min_{|\Psi\rangle \rightarrow \rho} \langle \Psi | \mathbf{T} + \mathbf{V}_{ee} | \Psi \rangle \quad (1.49)$$

$\mathcal{F}$ is the *universal functional*. Using the classical Coulomb expression (E_J)

$$E_J[\rho_0(\vec{r})] = \frac{1}{2} \iint d\vec{r} d\vec{r}' \frac{1}{|\vec{r} - \vec{r}'|} \rho(\vec{r}) \rho(\vec{r}') \quad (1.50)$$

we may further decompose the universal functional into kinetic (T), Coulomb (E_J) and the undetermined parts (XC) associated with non-classical exchange and correlation effects

$$\mathcal{F}[\rho_0(\vec{r})] = T[\rho_0(\vec{r})] + E_J[\rho_0(\vec{r})] + XC[\rho_0(\vec{r})] + \int d\vec{r} V_{\text{ext}} \rho_0(\vec{r}) \quad (1.51)$$

1.2.3 The Kohn-Sham Formulation of DFT

Despite its simple looking form, Eq. (1.51) still poses tremendous challenges. The first obstacle is that finding an accurate form for the kinetic energy functional $T[\rho_0(\vec{r})]$ remains an unsolved challenge to the present. In the early days, Thomas, [71] Fermi [72] and Dirac [73] first derived a tractable analytical form of the kinetic energy functional T from the uniform electron gas (UEG) model. However, this crude approximation to reality resulted in estimates that did not predict chemical binding, a critical aspect of chemistry. Research efforts focused on modeling accurate kinetic energy density functionals (KEDF) continue in the 21st century, [74, 75] but achieving chemical accuracy with pure KEDFs remains challenging.

In 1965, Kohn and Sham proposed to circumvent this problem by introducing a fictitious system of *non-interacting electrons* that replicates the same density as the real, fully-interacting

system. [76] Consider the determinantal wavefunction of this fictitious system $|\Phi^{\text{KS}}\rangle$, constructed from the set of Kohn-Sham orbitals $\{\phi_i^{\text{KS}}\}$. We write its density

$$\rho_0(\vec{r}) = \rho^{\text{KS}}(\vec{r}) = \sum_i |\phi_i^{\text{KS}}(\vec{r})|^2 \quad (1.52)$$

and the corresponding kinetic energy contribution from this fictitious Kohn-Sham state may be exactly evaluated as

$$T^{\text{KS}}[\rho_0(\vec{r})] = T^{\text{KS}}[\rho^{\text{KS}}(\vec{r})] = -\frac{1}{2} \sum_i \langle \phi_i^{\text{KS}} | \nabla^2 | \phi_i^{\text{KS}} \rangle \quad (1.53)$$

Based on this, we rewrite the ground state energy functional by reintroducing orbitals into the expression

$$E_0[\rho_0(\vec{r})] = T^{\text{KS}}[\rho_0(\vec{r})] + E_J[\rho_0(\vec{r})] + XC[\rho_0(\vec{r})] + \left(T[\rho_0(\vec{r})] - T^{\text{KS}}[\rho_0(\vec{r})] \right) + \int d\vec{r} V_{\text{ext}} \rho_0(\vec{r}) \quad (1.54)$$

One can largely draw a parallel between $XC + T - T^{\text{KS}}$ with the exchange and correlation contributions in wavefunction quantum chemistry. Thus, we define the *Kohn-Shan exchange-correlation* functional

$$E_{\text{xc}} \equiv XC[\rho^{\text{KS}}(\vec{r})] + \left(T[\rho_0(\vec{r})] - T^{\text{KS}}[\rho^{\text{KS}}(\vec{r})] \right) \quad (1.55)$$

$$\equiv E_{\text{x}}[\rho_0(\vec{r})] + E_{\text{c}}[\rho_0(\vec{r})] + \left(T[\rho_0(\vec{r})] - T^{\text{KS}}[\rho^{\text{KS}}(\vec{r})] \right) \quad (1.56)$$

These results show that in principle, if the exact form of the exchange-correlation functional can be determined, we can obtain the exact ground state energy of a system using ρ_0 , which only depends on 3 spatial degrees of freedom regardless of the system size!

Assuming we obtain an expression for E_{xc} , how may we obtain ρ_0 using the Kohn-Sham formulation? Variation of T^{KS} with respect to ρ_0 is ill-defined, but we may instead perform a functional derivative with respect to the fictitious Kohn-Sham orbitals $\{\phi_i^{\text{KS}}\}$. That is, assuming a differential change in the orbitals $\phi_i^{\text{KS}} \rightarrow \phi_i^{\text{KS}} + \delta\phi_i^{\text{KS}}$, we write the functional derivative of E_0 with respect to $(\delta\phi_i^{\text{KS}})^*$:

$$\frac{\delta E_0}{\delta \phi_i^{\text{KS}*}(\vec{r})} = \frac{\delta T^{\text{KS}}}{\delta \phi_i^{\text{KS}*}(\vec{r})} + \left[\frac{\delta E_{\text{ext}}[\rho_0(\vec{r})]}{\delta \rho_0(\vec{r})} + \frac{\delta E_J[\rho_0(\vec{r})]}{\delta \rho_0(\vec{r})} + \frac{\delta E_{\text{xc}}[\rho_0(\vec{r})]}{\delta \rho_0(\vec{r})} \right] \frac{\delta \rho_0(\vec{r})}{\delta \phi_i^{\text{KS}*}(\vec{r})} = 0 \quad (1.57)$$

where the chain rule is applied for the terms that directly depend on ρ_0 . With the Lagrange multiplier ϵ_i which enforces orthonormality of the Kohn-Sham orbitals, $\langle \phi_i^{\text{KS}} | \phi_j^{\text{KS}} \rangle = \delta_{ij}$, as well as $\delta \rho_0 / \delta (\phi_i^{\text{KS}})^* = \phi_i^{\text{KS}}$, we obtain the *Kohn-Shan equations*

$$\left[-\frac{1}{2} \nabla_i^2 + v_{\text{eff}}(\vec{r}) \right] \phi_i^{\text{KS}}(\vec{r}) = \epsilon_i(\vec{r}) \phi_i^{\text{KS}}(\vec{r}) \quad (1.58)$$

where the effective potential $v_{\text{eff}}(\vec{r})$ is defined

$$v_{\text{eff}}(\vec{r}) \equiv v_{\text{ext}}(\vec{r}) + \int d\vec{r}' \left(\frac{\rho_0(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{xc}[\rho_0(\vec{r})]}{\delta \rho_0(\vec{r})} \right) \quad (1.59)$$

This effective potential is dependent on the Kohn-Sham orbitals through second (Coulomb) and third (exchange-correlation) contributions. Therefore, (1.58) must be solved self-consistently.

Let us compare Hartree-Fock and the Kohn-Sham equations (Eqs. (1.31) and (1.58)). Both are eigenvalue equations that must be solved self-consistently. Therefore, the same approach can be used to solve both sets of equations. The most popular approach introduces atomic orbitals to represent each molecular orbital as a linear combination of atomic orbitals (LCAO). Both formalisms also describe the multi-electron system with a single determinant, but the Kohn-Sham equations include the effect of electron correlation via the exchange-correlation functional E_{xc} while Hartree-Fock equations do not include electron-correlation (and therefore usually yields less accurate predictions). In addition, Eq. (1.31) requires evaluation of the two-electron terms $\mathbf{J}$ and $\mathbf{K}$, while (1.31) may not require $\mathbf{K}$ depending on the form of E_{xc} (see Sec. 1.2.4). The computational cost of solving the Hartree-Fock equation scales formally as $O(N^4)$ with respect to system size N due to the two-electron integrals required for $\mathbf{J}$ and $\mathbf{K}$, whereas solving the Kohn-Sham equation may only cost $O(N^3)$ scaling with the simplest form of E_{xc} , though more sophisticated forms of E_{xc} may cost $O(N^4)$ or more (See Sec. 1.2.4).

1.2.4 Jacob’s Ladder of DFT: Search for the Perfect E_{xc}

Until now, we have made no approximations. We have used a divide-and-conquer approach to study the universal functional $\mathcal{F}$, and the only part unknown under the KS formalism is E_{xc} . The question remains: do we have the exact E_{xc} ? The answer is no, and we will likely never know it.

Nevertheless, several practical *Density Functional Approximations* (DFAs) are accurate enough to be useful in chemistry. In fact, a few hundred DFAs have been devised over the past few decades, [77–79] a state which Kieron Burke has described as the “Alphabet Soup” of exchange-correlation functionals. [78] Some of these DFAs show comparable performance to correlated wavefunction theories such as MP2. Interested readers should review Ref. [77] which provides an extensive review of the efforts in DFA development during the past few decades.

The DFAs may be grouped by their levels of sophistication and the approximations used to create them. John Perdew has proposed the concept of the Jacob’s Ladder of DFT, which extends from the “earth” of the Hartree-only world without exchange-correlation to “heaven” with a complete description of exchange-correlation to achieve chemical accuracy. [80] Jacob’s Ladder bridges the two realms, and the ascent of a rung in this ladder represents a systematic improvement in the level of approximation and potentially also the accuracy of E_{xc} , relative to the rung below it. Fig. 1.1 provides a visual representation of the ladder. Here we will review each rung of Jacob’s Ladder and the performances of some representative from the bottom up.

Rung 1: Local Density Approximation (LDA). The functionals at the lowest rung of the Jacob’s Ladder are the Local Density Approximation (LDA) functionals. These functionals assume that

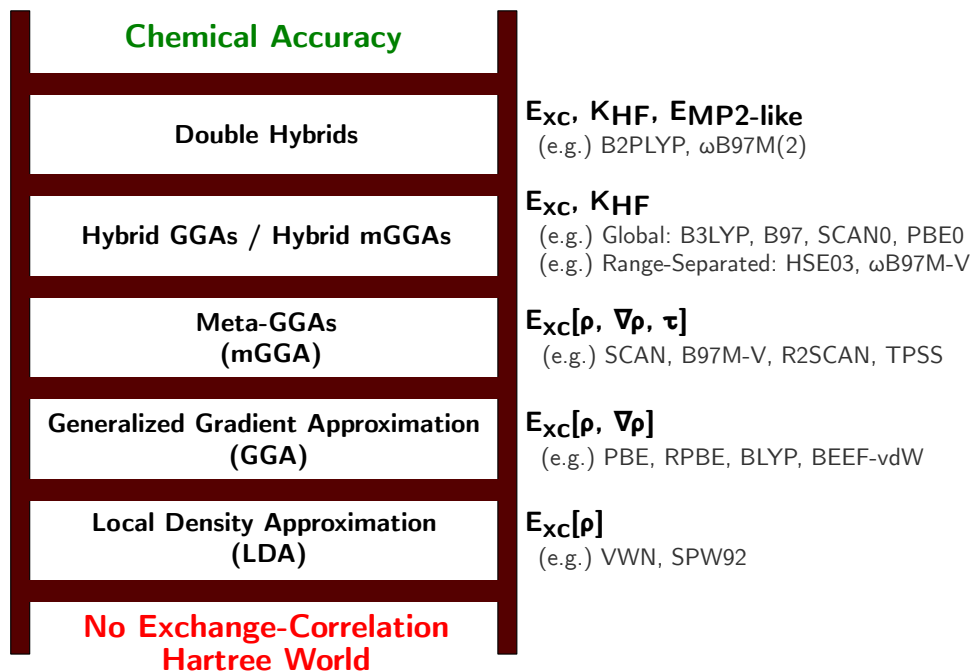


Figure 1.1: Jacob’s Ladder for Density Functional Approximations. Key components of each rung and a few representative DFAs are listed at the right of the ladder.

E_{xc} can be modeled as

$$E_{xc}^{\text{LDA}} = \int d\vec{r} \rho(\vec{r}) \varepsilon_{xc}^{\text{LDA}}(\rho) \quad (1.60)$$

where $\varepsilon_{xc}(\rho)$ only depends on the value of the density at point $\vec{r}$. An exact form of the exchange functional (E_x of Eq. (1.56)) of E_{xc} can be derived for the UEG, [69] which is $\varepsilon_{xc}(\rho) = -\frac{3}{4}[3\rho/\pi]^{1/3}$ (while the remaining correlation term must still be modeled by fits to high accuracy UEG calculations using quantum Monte Carlo methods) [81, 82]. We may further assume that the functional may depend separately on the alpha- and beta-spin densities. This leads to the local spin density approximation (LSDA)

$$E_{xc}^{\text{LSDA}} = \int d\vec{r} \rho_\alpha(\vec{r}) \varepsilon_{xc}^\alpha(\rho_\alpha) + \int d\vec{r} \rho_\beta(\vec{r}) \varepsilon_{xc}^\beta(\rho_\beta) \quad (1.61)$$

For the UEG, $\varepsilon_{xc}^\alpha(\rho) = \varepsilon_{xc}^\beta(\rho) = -\frac{3}{2}[3\rho/4\pi]^{1/3}$, and this is called the Slater exchange. [83] Examples of LSDA models include SVWN [84] and SPW92 [85]. As this is the crudest form of DFA, the functionals in this rung perform significantly worse than chemical accuracy. For example, when tested on the non-covalent easy molecular cluster dataset (NCEC), SPW92 has a root mean square deviation (RMSD) error of ≈ 38 kcal/mol. This set is comprised of 243 binding energies of molecular clusters, including water trimers to 20-mers, ammonia clusters, hydrogen fluoride

clusters, and solvated anions. [77] For difficult thermochemistry dataset (TCD) which has 258 data points of atomization, bond dissociation, and heavy-atom transfer energies, [86] SPW92 results in an RMSD of ≈ 65 kcal/mol. [77]

Rung 2: Generalized Gradient Approximation (GGA). In the spirit of the Taylor expansion, DFAs in the second lowest rung of the Jacob’s Ladder include direct dependence on $\nabla\rho$ directly into E_{xc} . These are called the Generalized Gradient Approximation (GGA) functionals

$$E_{xc}^{\text{GGA}} = \int d\vec{r} \rho(\vec{r}) \varepsilon_{xc}^{\text{GGA}}(\rho, \nabla\rho) \quad (1.62)$$

GGA functionals can be categorized into empirical and non-empirical functionals. The non-empirical functionals include PBE [87] and RPBE [88]. These functionals do not contain parameters fit to experiment but instead the functional form and associated parameters are chosen to obey a limited set of exact conditions. For example, RPBE has enjoyed good success in the materials modeling community for its fair prediction of adsorption energies and interfacial interactions (< 5 kcal/mol mean absolute error in chemisorption energies compared to experiment). [88, 89] On the other hand, semi-empirical functionals contain empirical parameters fitted against benchmark data. These include BLYP, [90] BEEF-vdW, [91] and B97-D3. [92] GGA functionals can yield orders of magnitude improvements over LDA/LSDA functionals. For example, the B97-D3 functional yields an RMSD of ~ 5 kcal/mol on the NCEC dataset and an RMSD of ~ 8 kcal/mol on the TCD dataset, errors that are 5-10 times smaller than SPW92.

Rung 3: Meta-Generalized Gradient Approximation (mGGA). The next natural step is to include Hessians of the density $\nabla^2\rho$. However, the more common approach is to include the kinetic energy density [93] instead defined as

$$\tau(\vec{r}) = \sum_i \left| \vec{\nabla} \phi_i(\vec{r}) \right|^2 \quad (1.63)$$

where $\sigma \in [\alpha, \beta]$.¹ One can show that the kinetic energy density τ and $\nabla^2\rho$ are related, so in principle either choice could be used in practice. [93] Choosing the kinetic energy density leads to the following form for E_{xc}

$$E_{xc}^{\text{mGGA}} = \int d\vec{r} \rho(\vec{r}) \varepsilon_{xc}^{\text{mGGA}}(\rho, \vec{\nabla}\rho, \tau) \quad (1.64)$$

Popular examples of non-empirical mGGA functionals include TPSS [94] and SCAN. [95] SCAN has particularly enjoyed success in the solid-state and condensed matter physics community, and its improved versions (e.g., r^2 SCAN [96]) have been developed. Both functionals are designed to satisfy all or a subset of exact conditions for mGGA approximations. By contrast, the semi-empirical, combinatorial-designed B97M-V functional [97] has shown significantly better performance for molecular chemistry within this rung. [77] B97M-V has RMSDs of 0.95 kcal/mol and 4.82 kcal/mol when evaluated on NCEC and TCD datasets, respectively. [77]

¹ τ is not to be confused with the spin-coordinates used in Slater Determinants.

Rung 4: Hybrid Functionals. The functionals at rungs 1-3 often exhibit systematic errors due to limitations in the functional form used for E_{xc} . To see one of the limitations, let us revisit the form of E_J

$$E_J[\rho_0(\vec{r})] = \frac{1}{2} \iint d\vec{r} d\vec{r}' \frac{1}{|\vec{r} - \vec{r}'|} \rho(\vec{r}) \rho(\vec{r}') \quad (1.65)$$

A keen reader may notice that there is no restriction in the interaction of the of two densities. Compare this with the equivalent term in the Hartree-Fock Equation (Eq. (1.29)) — one finds that HF includes a restricted summation where two occupied orbitals indices must be different. Eq. (1.65) does not have such a restriction, and E_J thus includes a spurious interaction term between an electron and itself. This term in principle must be canceled by the exact form of E_{xc} . However, because we do not know the exact form of E_{xc} , some fictitious self-interaction contributions are left uncanceled, resulting in the infamous *self-interaction error* (SIE). [98–101] SIE can substantially impact the accuracy of the functionals in rungs 1-3 that are only dependent on the local information at a given point. For example, SIE leads to significant underestimation of the reaction barriers and over-delocalization of the charge distribution. Further details of the self-interaction error and its associated pitfalls are given in refs. [102–106].

One strategy to reduce the SIE is by explicitly including some Hartree-Fock exchange-like terms (i.e., K_{ij} , Eq. (1.30)), often called “exact-exchange” in DFAs. This idea was pioneered in the early 1990s, when Becke introduced the idea of mixing a global fraction of exact exchange, [107, 108] which can be justified with the adiabatic connection theorem. [109–112] These global hybrid (GH) functionals take the form of

$$E_{xc}^{GH} = -\frac{1}{2} \sum_{ij} c_x K_{ij} + (1 - c_x) E_x + E_c \quad (1.66)$$

Global hybrid functionals can also be either non-empirical (e.g., PBE0 [113]) or empirical (e.g., B3LYP [107]). Using D3 dispersion corrections [92], PBE0 and B3LYP yield RMSDs of 8.72 and 5.97 kcal/mol for the TCD dataset, respectively. These mark a significant improvement over their GGA versions which have RMSDs of 17.20 and 11.11 kcal/mol with the same correction [77]. Eq. (1.66) can be applied to mGGAs as well, which will lead to hybrid mGGAs. Examples of this type of functional include MO6-2X, [114] TPSSh [115], and SCAN0 [116].

More sophisticated hybrid functionals include range-separation. [117, 118] These functionals split the K contribution into short- and long-range components by incorporating an error function into Eq. (1.30). The split between short-range and long-range interaction is governed by parameter ω

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \underbrace{\frac{1 - \text{erf}(\omega|\vec{r}_1 - \vec{r}_2|)}{|\vec{r}_1 - \vec{r}_2|}}_{\text{Short Range}} + \underbrace{\frac{\text{erf}(\omega|\vec{r}_1 - \vec{r}_2|)}{|\vec{r}_1 - \vec{r}_2|}}_{\text{Long Range}} \quad (1.67)$$

One may employ this form to evaluate K_{sr} and K_{lr} for short-range and long-range contributions. Using this, the range-separated hybrid (RSH) functionals takes the following form:

$$E_{xc}^{\text{RSH}} = -\frac{1}{2} \sum_{i,j} (c_{x,\text{sr}} K_{ij,\text{sr}} + c_{x,\text{lr}} K_{ij,\text{lr}}) + (1 - c_x) E_x + E_c \quad (1.68)$$

RSH functionals have better accuracy than the GHs due to lower SIE than the GHs and are very popular. As an example, the modern ω B97M-V functional (which used semi-empirical combinatorial functional design) [119] has an RMSE of 4.3 kcal/mol on the TCD dataset. As a testament to the quality of its performance for diverse chemical problems, ω B97M-V has also been used to generate large-scale benchmark training databases (e.g., OMol25, OPoly26) [120, 121] as well as training data for modern machine-learning interatomic potentials [68, 122] (e.g., MACE-OFF [123] and MACE-POLAR [124]). Finally, at the cost of accuracy for molecular chemistry, it is possible to entirely remove the long-range part of the expression, to obtain a screened exchange functional. [125, 126] A popular choice for such an approach is the HSE family of functionals, which is often used in extended systems (e.g., HSE03, [127] HSE06, [128] and HSEsol [129]), all of which are aimed at reducing the compute cost of exact exchange for solids and avoid artifacts of exact exchange for metals.

Rung 5: Double Hybrids and Beyond. The functionals of rung 5 attempt to add more wavefunction-like character to DFAs. At present, commonly used double-hybrid functionals (DH) [130] generally take the form of

$$E_{xc}^{\text{DH}} = -\frac{1}{2} \sum_{ij} c_1 K_{ij} + (1 - c_1) E_x + c_2 E_{\text{MP2-like}} + (1 - c_2) E_c \quad (1.69)$$

where $E_{\text{MP2-like}}$ is the correlation energy computed from MP2 theory using unoccupied Kohn-Sham orbitals. Even with that rough approximation for non-local correlation, DHs are generally among the most accurate functionals. Indeed, ω B97M(2) presents a remarkable error of 2.71 kcal/mol for the TCD dataset. [131] DHs however also incur increased computational cost due to the explicit evaluation of $E_{\text{MP2-like}}$, which requires wavefunction correlation energies. Nevertheless, recent developments in DHs have been showing encouraging results in conjunction with regularized forms of the MP2 contribution. [132–135]

1.3 Quantum Chemistry for X-ray Spectroscopy

How do we characterize, quantify, and investigate the intermediates and their changes in a catalytic process? One technique that has become increasingly popular for heterogeneous catalysis is X-ray spectroscopy. [136–138] X-ray photons can excite or ionize core-level electrons. The advantage of probing core-level electrons is that their excitation and ionization energies usually lie within a characteristic range. Within a given range, the change in the energies occur through the interaction with the surrounding environment, which in turn yields local information such as oxidation states

of the element. [139–141] In recent years, there have been significant advances in using table-top experimental apparatus to generate pulses that can probe core-electrons. One of the most famous example of such development is the high harmonic generation. [142–144]

The two lowest energy levels that can be targeted in an X-ray spectra are K-edges (i.e., ionization/excitation of $1s$ orbital) and L-edges (i.e., ionization/excitation of $2s, 2p$ orbitals). K-edge does not require any spin-orbit coupling due to selection rules. However, $1s$ electrons are more tightly bound to the core, and its ionization/excitation requires higher energy pulses, which makes L-edge spectra more accessible for experiments. On the other hand, theoretically modeling ionization/excitation from $2p$ -type orbitals requires treatment of spin-orbit coupling. The latter aspect will be rigorously discussed in Chapter 2.

In this section, we review quantum chemical theories that can be used to compute ionization and excitations from core-electron levels. We first review approaches that begin from ground state solutions and then state-specific approaches that utilize orbital-optimization. In addition, we review the Dirac equation as a gentle introduction to relativistic effects that are important for core-electrons. We limit our focus to mean-field methods: DFT and HF.

1.3.1 From the Ground State Solution

The simplest way to model core-electron spectroscopy is to start from a ground state solution. For ionization, we can use *Koopman's Theorem*. Once self-consistency is reached, each orbital will have its corresponding canonical eigenvalue. We can simply take the negative of the eigenvalue of $|\chi_i\rangle$ that we are interested in: $-\epsilon_i$ to approximate the IP.

For excitations, we may first focus on using the ground state Hartree-Fock orbitals as building blocks. This is the starting point for *Configuration Interaction Singles* (CIS). [145, 146] *Brillouin's Theorem* states that the ground state HF determinant $|\Phi_0\rangle$ does not interact with singly excited determinants $|\Phi_i^a\rangle$

$$\langle \Phi_0 | \mathcal{H}_e | \Phi_i^a \rangle = 0 \quad (1.70)$$

We can therefore use the set of singly excited determinants as a many-electron basis for representing excited states

$$|\Psi_{\text{CIS}}\rangle = \sum_i^a t_i^a |\Phi_i^a\rangle \quad (1.71)$$

as this multi-determinant wavefunction is strictly orthogonal to the ground state. Their amplitudes t_i^a are computed by making matrix elements of the multi-electron Hamiltonian $\mathcal{H}_e$ in the basis of singly-excited determinants

$$\mathcal{H}_{ia,jb} \equiv \langle \Phi_i^a | \mathcal{H}_e | \Phi_j^b \rangle = (\epsilon_a - \epsilon_i) \delta_{ia} \delta_{jb} + \langle ij | ab \rangle - \langle ij | ba \rangle \quad (1.72)$$

and diagonalizing it.

Similar approach in DFT is the *linear-response time-dependent density functional theory* (LR-TDDFT). In order to introduce LR-TDDFT, we first review the explicitly time-dependent formulation of DFT (also called real-time TDDFT). The Runge-Gross theorem, the time-dependent analogue of the HK theorem, states that the exact time-dependent electronic density $\rho(\vec{r}, t)$ determines the time-dependent external potential $V_{\text{ext}}(\vec{r}, t)$ up to a position-independent constant. [147] Practical real-time TDDFT involves an additional adiabatic approximation, which assumes that the exchange-correlation functional E_{xc} is independent of time [148, 149] (We note the adiabatic approximation may be inappropriate and its limitations are evident in some applications [150]). This leads to the time-dependent Kohn-Sham equations (TDKS) [148, 151]

$$i \frac{d}{dt} \phi_i^{\text{KS}}(\vec{r}, t) = \mathbf{F}^{\text{KS}} \phi_i^{\text{KS}}(\vec{r}, t) \quad (1.73)$$

which governs how the Kohn-Sham orbital ϕ_i^{KS} evolves over time t . The operator $\mathbf{F}^{\text{KS}}$ is the time-dependent Kohn-Sham operator

$$\mathbf{F}^{\text{KS}}(t) = -\frac{1}{2} \nabla_i^2 + V_{\text{ext}}(\vec{r}, t) + \int d\vec{r}' \frac{\rho_0(\vec{r}', t)}{|\vec{r} - \vec{r}'|} + \frac{\delta A_{xc}}{\delta \rho_0(\vec{r}, t)} \quad (1.74)$$

A_{xc} is the time-dependent analogue of E_{xc} .²

TDDFT can be used to model excited states under the linear response framework. [152] Assume that a molecule is subject to a time-dependent AC field. We may model the change in the ground state density in terms of its linear response using the frequency-dependent polarizability. The poles of the response are Bohr Frequencies ω , which is directly related to excitation energies. Under this approximation, LR-TDDFT excitation energies can be obtained by solving through a non-Hermitian eigenvalue problem known as *Casida's equation* [153]

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \quad (1.75)$$

where $\mathbf{A}$ and $\mathbf{B}$ are defined for semi-local functionals (rungs 1-3) as

$$A_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ia} \delta_{jb} + \langle ij | ab \rangle + \langle ij | f_{xc} | ab \rangle \quad (1.76)$$

$$B_{ia,jb} = \langle ib | aj \rangle + \langle ib | f_{xc} | aj \rangle \quad (1.77)$$

For hybrid functionals, $\mathbf{A}$ and $\mathbf{B}$ are

$$A_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ia} \delta_{jb} + \langle ij | ab \rangle - c_{\text{HF}} \langle ia | jb \rangle + (1 - c_{\text{HF}}) \langle ij | f_{xc} | ab \rangle \quad (1.78)$$

$$B_{ia,jb} = \langle ib | aj \rangle - c_{\text{HF}} \langle ia | bj \rangle + (1 - c_{\text{HF}}) \langle ib | f_{xc} | aj \rangle \quad (1.79)$$

²The functional A , which serves as the quantum analogue of the classical action integral, incorporates A_{xc} as the time-dependent quantum counterpart to E_{xc} . See Ref. [152]

$\{\epsilon_p\}$ are the eigenvalues of the Kohn-Sham orbitals ϕ_p . $\langle ij|ab\rangle$ denotes the two-electron integral (c.f., Eq. (1.29)). c_{HF} represents the fraction of the exact exchange for a given hybrid functional. The exchange-correlation contribution is computed via

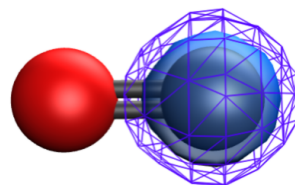
$$\langle ij|f_{xc}|ab\rangle = \iint d\vec{r} d\vec{r}' \phi_i^*(\vec{r})\phi_j^*(\vec{r}') \frac{\delta^2 E_{xc}}{\delta\rho(\vec{r})\delta\rho(\vec{r}')} \phi_a(\vec{r})\phi_b(\vec{r}') \quad (1.80)$$

To determine XAS spectra efficiently, one may limit the single excitation space and only include the relevant core orbitals, which is also known as the core-valence separation (CVS). [154, 155] Furthermore, one may assume that there is no de-excitation contribution in the linear response, which is equivalent to setting $\mathbf{Y} = 0$. This approximation is known as the Tamm-Dancoff approximation (TDA) [156] and reduces Eq. (1.75) to a Hermitian eigenvalue equation $\mathbf{A}\mathbf{X} = \omega\mathbf{X}$. LR-TDDFT/TDA is the most commonly applied form of TDDFT used to calculate excitation energies of a ground state system.

1.3.2 State-Specific Approaches

How does using a ground-state solution fare in estimating ionization/excitation for a core-electron? Let us assess the approach by computing the carbon K-edge ionization potential (IP) for a CO molecule in the gas phase. The experimental value is reported to be 296.2 eV. [157] Applying the Koopman's theorem with the SCAN [95] functional and Dunning's quadruple-zeta correlation consistent basis set with tight-core, diffuse and polarized functions (i.e., aug-cc-pCVQZ) [158–161] yields the estimated K-edge IP of 276.28 eV. This is ≈ 20 eV lower than the actual experimental value!

Instead of using the ground state solution, one can attempt to optimize a determinant for a non-Aufbau electronic configuration directly. Ref. [162] shows that given an exact ground state functional $E[\rho(\vec{r})]$, every density $\rho(\vec{r})$ that is an extrema in E with respect to $\delta\rho$ corresponds to an excited state (although the reverse is not true). Thus one may optimize an extrema density ρ' corresponding to a non-Aufbau configuration, compute its energy, and obtain the energy difference between two determinants to get the IP. This procedure is known as Δ -SCF in the literature. [163] Performing this calculation on CO with the same level of theory (SCAN/aug-cc-pCVQZ), we obtain 296.45 eV which is a significant improvement over Koopman's theorem! Fig. 1.2 shows the change in the 1s-electron orbital before and after orbital-optimization (i.e., the ground state vs 1s-ionized, orbital-optimized non-Aufbau configuration). It shows that the 1s-orbital has contracted substantially such that a ground state density is no longer a good representation of it. Physically, this reflects increased



Lines: Ground State C 1s
Surface: Core-hole Optimized C 1s

Figure 1.2: Comparison of two 1s-orbitals in ground state (purple, meshed surface) vs 1s-ionized non-Aufbau configuration (blue, solid surface). Both isosurfaces contain 99% of electronic density.

effective nuclear charge in the core ion due to loss of the 1s electron. A detailed analysis on the performance of Δ -SCF methods and OO-approaches can be found in Refs. [140] and [164].

One of the main challenges of OO methods is to converge to the target extrema with respect to orbital variation θ . In fact, while OO methods predate LR-TDDFT/TDA in the literature, [163, 165–167] they have received less attention due to this difficulty. Optimization of extrema may suffer *variational collapse*, which occurs when the SCF iterations converge to much lower energy local minima. [140, 168] Nevertheless, recent theoretical developments allow better convergence to desired target densities. Here we list a few commonly employed algorithms:

1. *Maximum Overlap Method* (MOM) [169]: For the k -th iteration in the self-consistency loop, MOM computes the projection of each orbital ϕ_j onto the occupied orbitals of the $(k-1)$ -th iteration:

$$p_j = \sqrt{\sum_i^N \left| \langle \phi_i^{(k-1)} | \phi_j^{(k)} \rangle \right|^2} \quad (1.81)$$

After the full set of p_j is computed, MOM chooses the next set of occupied orbitals based on the N -largest p_j values. MOM remains one of the most popular algorithms for obtaining non-Aufbau configurations. The original implementation of MOM can itself occasionally undergo variational collapse, as it only computes the projected norm with respect to the previous step. An improvement can be made by always projecting back to the initial guess set of orbitals $\{\phi_i^{(0)}\}$:

$$p'_j = \sqrt{\left(\sum_i^N \left| \langle \phi_i^{(0)} | \phi_j^{(k)} \rangle \right|^2 \right)} \quad (1.82)$$

which can anchor the subsequent SCF iterations to the initial guess. This procedure is known as IMOM and has shown better performance over MOM, [170] although it does not completely prevent variational collapse. [164]

2. *Square Gradient Minimization* (SGM) [171]: A few approaches characterize saddle points on PESs by recasting the extremization problem as a minimization problem using the square of the potential energy gradient. [172–175] SGM applies the same strategy in θ -space, thereby minimizing the following objective function

$$\Delta \equiv |\nabla_{\theta} \mathcal{L}^2| = \sum_{ia} \left| \frac{\partial \mathcal{L}}{\partial \theta_{ia}} \right|^2 \quad (1.83)$$

where θ_{ia} represents the orbital mixing between occupied orbital i and virtual orbital a and $\mathcal{L}$ is the Lagrangian for energy functional. This method demonstrates superior performance compared to MOM/IMOM, particularly for restricted open-shell calculations. [171, 176, 177] However, Δ minimization is ill-conditioned. Increasing the number of basis functions therefore increases the condition number and cause poor results or convergence to unwanted saddle points.

3. *State-Targeted Energy Projection* (STEP) [178]: STEP applies a level shift to the virtual orbitals in order to ensure desired non-Aufbau occupation and restrict orbital mixings that may lead to variational collapse. The shift effectively places the core-hole above the highest occupied molecular orbital (HOMO) of the non-Aufbau configuration. The projection operator $\mathbf{Q}$ is defined

$$\mathbf{Q} = \sum_a^{\text{virt}} |\phi_a\rangle \langle \phi_a| \quad (1.84)$$

Adding this to the Fock operator leads to the modified Fock matrix

$$\mathbf{F}' = \mathbf{F} + \eta \mathbf{S} \mathbf{Q} \mathbf{S} \quad (1.85)$$

where shift η is anchored to the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)

$$\eta = |\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}| + \epsilon' \quad (1.86)$$

with a user-defined parameter ϵ' . STEP does demonstrate faster convergence than SGM and more robust performance than MOM/IMOM. In practice, STEP requires a large value of ϵ' for core-hole states to ensure a strong enough anchoring. This may result in much slower convergence. STEP is also more prone to suffer from variational collapse compared to SGM.

In this dissertation, we employ SGM to converge obtain core-ionized or core-excited determinants, in order to obtain spin-pure, restricted open-shell solutions.

1.3.3 The Middle Ground

OO methods are not “black-box.” In order to compute the final state, one must have some prior knowledge such as its spin state and electronic configuration. This is a key drawback, particularly when one is interested in excitations without prior knowledge of the process. Ref. [164] presents a thorough review of existing challenges in OO-DFT. For this reason, a “middle-ground” approach that can include both orbital-optimization and linear-response-like character is desired.

One approach that accomplishes both task is the *static exchange* (STEX) method. [179, 180] To model K-edge excitations, for instance, STEEX obtains a non-Aufbau solution for a core-ion with a $1s$ hole. Then one computes the excitation energies by subsequently diagonalizing the virtual space of a Fock matrix. An analogue within LR-TDDFT for closed-shell references has also been developed, is called Electron-Affinity TDDFT (EA-TDDFT). [181]

A generalization of this approach is the Non-orthogonal CIS (NOCIS) method developed by Head-Gordon and co-workers which can include more than one core-ionized determinants as well as coupling between them. [182–184] NOCIS also projects its wavefunction against the neutral

ground state in order to maintain the strict orthogonality with the ground state demonstrated by the Brillouin's Theorem in a CIS wavefunction. Thus the NOCIS wavefunction is

$$|\Psi_{\text{NOCIS}}\rangle = \sum_{i=1}^R \sum_{a=1}^V t_i^a (1 - \mathbf{P}) |\Phi_i^a\rangle \quad (1.87)$$

where R is the number of ionized and orbital-optimized references, V is the number of virtual orbitals for each reference and $\mathbf{P} = 1 - |\Phi_0\rangle\langle\Phi_0|$ (i.e., projecting out the GS contribution). In practice, the amplitudes of each singly-excited determinants t_i^a are obtained by evaluating the multi-electron Hamiltonian in the basis of GS-projected references

$$\mathbf{H}t_k = \mathbf{S}t_k E_k \quad \text{where} \quad H_{ia,jb} = \langle\Phi_i^a| (1 - \mathbf{P})^\dagger \mathcal{H}_e (1 - \mathbf{P}) |\tilde{\Phi}_j^b\rangle \quad (1.88)$$

and subsequently solving the generalized eigenvalue problem. Also, the sets of orbitals within Φ and $\tilde{\Phi}$ are non-orthogonal to each other. Computing matrix elements $H_{ia,jb}$ therefore requires either generalized Wick's Theorem [185] or generalized Slater-Condon rules. The latter can be computed either using matrix cofactors between determinants [186] or via transformed, bi-orthogonalized orbitals [187, 188] (also known as Löwdin Pairs or corresponding orbitals). [189, 190] NOCIS was initially implemented to closed-shell references, but it has subsequently been generalized to open-shell doublet and triplet ground state configurations, under the assumption that coupling between core-excitations with different excitation centers can be ignored (the one-center approximation, i.e., 1C-NOCIS). [183, 184] A rigorous generalization of NOCIS to DFT remains elusive, as coupling between two non-orthogonal determinants (and their densities) is not-defined in KS-DFT.

1.3.4 Relativistic Effects

A key consideration in calculation of core-electron spectroscopy is the treatment of relativistic effects. While mostly irrelevant for light elements, relativistic effects become more and more important for heavier transition metals, influencing even properties controlled by valence electrons such as the color of gold, [191] performance of Pb batteries, [192] or state of Hg at room temperature. [193] For core-electrons, relativistic effects are important even for main group elements because they are tightly bound to the nuclei such that their average speed is no longer a negligible fraction of the speed of light. Therefore, successful methods for calculating core level ionization and excitations must include relativistic effects, in addition to employing sufficiently accurate excited state methods that include orbital-optimization. [194]

While a rigorous presentation of relativistic quantum mechanics requires quantum field theory and quantum electrodynamics, here we limit our discussion to the simplest critical consideration: *Dirac's Equation* for a single particle. It is simple and quite detached from chemical systems, but it nonetheless provides the basic foundations necessary. For a more thorough presentation of relativistic quantum chemistry, we direct readers to Refs [195–198] and references therein.

In the special theory of relativity, the total energy of a free particle is written as

$$E = \sqrt{c^2|\vec{p}|^2 + m^2c^4} \quad (1.89)$$

where m is the rest mass of the particle, $|\vec{p}|$ is the norm of the momentum vector, and c is the speed of light. Instead of the total relativistic energy expression for E , it is often convenient to subtract out the contribution from the rest mass. Recall that to write a quantum analogue of Eq. (1.89), both classical momentum and energy must be replaced by corresponding operators $\vec{p}$ and $\mathbf{H}$. This, however, is complicated as the momentum operator must go under a square root. For example, Gordon suggested to take the square of the Hamiltonian [199]

$$\mathbf{H}^2 = c^2 \vec{p} \cdot \vec{p} + m^2 c^4 \quad (1.90)$$

$$\frac{\partial^2 |\psi\rangle}{\partial t^2} = -c^2 \vec{p} \cdot \vec{p} - m^2 c^4 \quad (1.91)$$

Writing Eq. (1.91) in spatial coordinates results in the *Klein-Gordon equation*. This equation satisfies the symmetry between time and space, treating them on equal footing, which is important for treatment of special relativity. However, solutions to Eq. (1.91) also allow negative probability densities, which is incompatible with the standard interpretation of quantum mechanics.

Dirac proposed to write the expression inside the radical as a perfect square of an expression that is linear in $\vec{p}$ such that the square root can be removed. We can write this expression as $c \vec{\alpha} \cdot \vec{p} + \beta m c^2$ and plug it into Eq. (1.90):

$$c^2 \vec{p} \cdot \vec{p} + m^2 c^4 = (c \vec{\alpha} \cdot \vec{p} + \beta m c^2)^2 = (c \alpha_x p_x + c \alpha_y p_y + c \alpha_z p_z + \beta m c^2)^2 \quad (1.92)$$

$$\begin{aligned} &= (c \alpha_x^2 p_x^2 + c \alpha_y^2 p_y^2 + c \alpha_z^2 p_z^2 + \beta^2 m^2 c^4) \\ &\quad + c^2 p_x p_y (\alpha_x \alpha_y + \alpha_y \alpha_x) + c^2 p_y p_z (\alpha_y \alpha_z + \alpha_z \alpha_y) + c^2 p_z p_x (\alpha_z \alpha_x + \alpha_x \alpha_z) \\ &\quad + m c^3 p_x (\alpha_x \beta + \beta \alpha_x) + m c^3 p_y (\alpha_y \beta + \beta \alpha_y) + m c^3 p_z (\alpha_z \beta + \beta \alpha_z) \end{aligned} \quad (1.93)$$

But expanding the left hand side of Eq. (1.90) yields

$$c^2 \vec{p} \cdot \vec{p} + m^2 c^4 = (c \alpha_x^2 p_x^2 + c \alpha_y^2 p_y^2 + c \alpha_z^2 p_z^2 + \beta^2 m^2 c^4) \quad (1.94)$$

To make both left hand sides of Eq. (1.93) and Eq. (1.94) be equal, $\vec{\alpha}$ and β must satisfy the following conditions

$$\alpha_i^2 = \beta^2 = 1 \quad (1.95)$$

$$\{\alpha_i, \alpha_j\} \equiv \alpha_i \alpha_j + \alpha_j \alpha_i = 0 \quad (1.96)$$

$$\{\alpha_i, \beta\} \equiv \alpha_i \beta + \beta \alpha_i = 0 \quad (1.97)$$

where $i, j \in [x, y, z]$ and the curly brackets $\{\cdot, \cdot\}$ denote the anti-commutator. It turns out that no one-dimensional quantity can satisfy Eqs. (1.95)-(1.97). In fact, the lowest dimensional objects that satisfy the conditions are four-dimensional. Thus Dirac proposed the following four-component spinor wavefunction to represent a relativistic free particle

$$\vec{\alpha} = \begin{bmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{bmatrix}, \quad \beta = \begin{bmatrix} I_2 & 0 \\ 0 & -I_2 \end{bmatrix} \quad \text{and} \quad \psi \mapsto (\phi_1, \phi_2, \chi_1, \chi_2) \quad (1.98)$$

such that

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} |\phi_1\rangle \\ |\phi_2\rangle \\ |\chi_1\rangle \\ |\chi_2\rangle \end{pmatrix} = (c\vec{\alpha} \cdot \vec{p} + \beta mc^2) \begin{pmatrix} |\phi_1\rangle \\ |\phi_2\rangle \\ |\chi_1\rangle \\ |\chi_2\rangle \end{pmatrix} \quad (1.99)$$

where $\vec{\alpha}$ corresponds to the 2×2 supermatrix based on each component of the standard Pauli matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (1.100)$$

and I_2 is the 2×2 identity matrix. This is the famous *Dirac equation*. Two observations can be made from the form of Eqs. (1.99) and (1.100): 1) including relativistic effects into the Hamiltonian quadruples the dimensionality of our problem, and 2) spin is inherently a relativistic effect, as Pauli matrices are closely tied with quantum mechanical spins.

The Dirac Hamiltonian can be scaled so that the rest mass contribution to the energy for the upper half can be zeroed. This makes to the lower half accumulate another $-mc^2$. In addition, the external one-body potential $\mathbf{V}$ (which would be $\mathbf{V}_{ne}$ for chemical applications) can be added perturbatively under the minimal coupling approximation. [196, 200] The one-particle Dirac Hamiltonian $\mathbf{H}_D$ can then be expressed as a 2×2 supermatrix

$$\psi = \begin{pmatrix} |\phi\rangle \\ |\chi\rangle \end{pmatrix}, \quad \mathbf{H}_D = \begin{pmatrix} \mathbf{V} & c \vec{\sigma} \cdot \vec{p} \\ c \vec{\sigma} \cdot \vec{p} & \mathbf{V} - 2mc^2 \end{pmatrix} \quad (1.101)$$

where $|\phi\rangle$ and $|\chi\rangle$ correspond to large and small components of the Dirac spinor. Solutions to Eq. (1.101) can be used to describe electrons or positrons, with the former having positive energy solutions with major amplitudes in $|\phi\rangle$, thus the name large component. However, both the large and small components are needed to describe electronic solutions fully. Modern relativistic quantum chemistry therefore builds upon Eq. (1.101) to include other necessary physics such as two-electron effects or dynamic correlation. Most active research direction in this area focuses on transforming the four-component Hamiltonian to two-component Hamiltonian, [201] either via approximation or exact via decoupling. [202–205] One such approach will be presented in Chapter 2.

1.4 DFT for Electrified Metal-Solution Interface

So far we reviewed foundational non-relativistic quantum chemistry and density functional theory. We also reviewed how these theories adapt when studying core-excited states, via the introduction of state-specific optimization and relativistic effects. In this section we shift gears to modeling elementary reactions occurring at the metal-solution interface and review various concepts from a

practitioner's point of view. The materials presented in this section will be relevant to Chapters 3 and 4.

To use DFT to simulate the solution-to-electrode interface, there are two important aspects one must adequately address: 1) selecting an effective but efficient computational model to approximate both electrode and solution that also 2) properly accounts for the applied potential and its impact on the overall non-neutral system. For this we first review the heterogeneous and complex nature of the electrode-electrolyte interface and present the computational strategies and theories for modeling.

1.4.1 Brief Overview of the Electrode-Electrolyte Interface

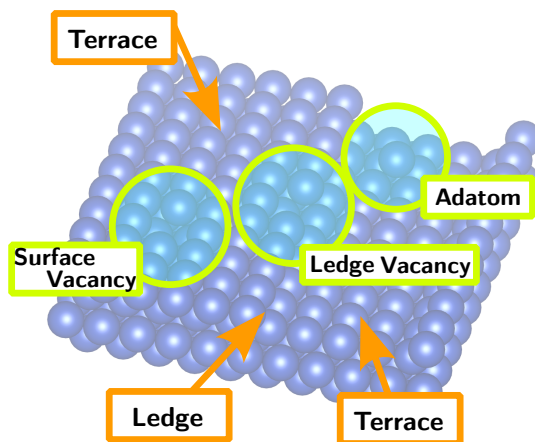


Figure 1.3: Schematic of the Terrace-Ledge-Kink (TLK) model for local surface morphology.

A typical interface is composed of the bulk metal, the *electrical double layer* (EDL), [206] and the bulk solution. The local characteristics of crystal surface are usually described by the terrace-ledge-kink (TLK) model (Fig. 1.3a). Some metal surfaces are best described by *grain boundaries*, an interface between two different surface orientations forming a bi-crystal structure. Realistic electrodes are however often amorphous, polycrystalline surfaces where a single facet is not an appropriate description. A bulk solution includes both solvent and electrolyte.

The electrical double layer (EDL) is the arrangement of the electrolyte and solvent in the region close to the electrode surface. A single unifying theory that can represent the EDL still remains difficult to formalize. As Schmickler points out in his perspective, Ref. [207], characterizing the EDL is challenged by connecting the microscopic theory of structure and macroscopic observables such as potential and capacitance. Nonetheless, notable microscopic features of the EDL can be explained based on the model proposed by Grahame in 1947, which builds upon previous works by Helmholtz, Gouy, Chapman and Stern. [206, 208] A schematic of this model is shown in Fig. 1.4a. First, adsorbed counter-ions without solvation shells or properly oriented solvent molecules form the *Inner Helmholtz Plane* (IHP), a layer on top of a planar electrode. In addition, fully solvated co-ions can approach the surface via non-covalent or electrostatic interactions. The

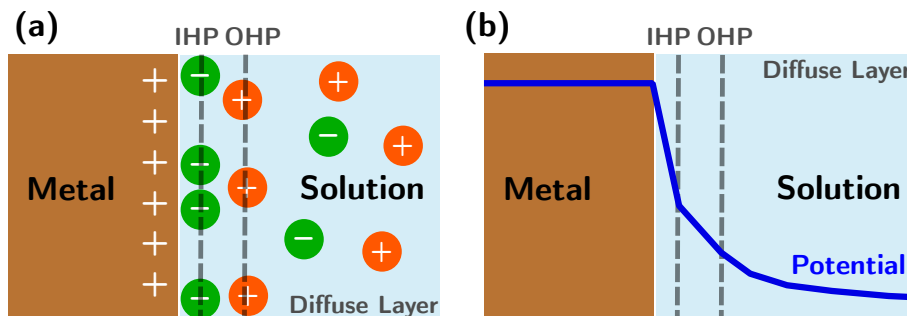


Figure 1.4: A schematic of the Electric Double Layer (EDL). Solvent molecules are not explicitly shown in this schematic. (a) Arrangement of the cation/anions on the charged metal surface. Location of the Inner and Outer Helmholtz Planes are noted by the dashed lines. (b) Schematic of the potential change across the electric double layer for a positively polarized metal surface.

closest approach of these solvated co-ions form the outer Helmholtz plane (OHP). Electrode, IHP, and OHP effectively form a layered capacitor, causing significant potential change from metal surface to OHP (Fig. 1.4b). [209] The thickness of the Helmholtz layers are subject to change based on the size of the electrolyte ions. [210] The remaining parts of the solution are often described as a diffuse layer with electrolyte concentration dominated by Boltzmann statistics. [211] This forms an exponential potential decay gradient, away from the metal electrode.

1.4.2 Modeling Interfaces with DFT

DFT can be very useful for simulating thermodynamics and kinetics of atomistic reactions occurring at the interface. In an ideal world, an explicit quantum mechanical description of every single atom in the simulation box is desired. This is however practically unattainable due to limited computational resources, even with modern high-performance computers, because of sampling challenges required by statistical mechanics and particle number bottleneck of DFT. Therefore, DFT-based modeling usually must still include additional approximations to limit the number of atoms explicitly simulated. In this dissertation, we mainly employ a single facet slab model with hybrid explicit/implicit solvation model, which we further elaborate below.

Designing the Slab Model. A solid surface preserving perfect crystal structure can be modeled under periodic boundary conditions (PBC). A crystal is composed of *lattice points*, an infinite set of points defined by integer sums of a set of linearly independent vectors. For a three dimensional crystalline structure, its primitive unit cell $\vec{R}$ has lattice vectors

$$\vec{R} = [\vec{a}_1, \vec{a}_2, \vec{a}_3] \quad (1.102)$$

Any point in the crystal structure can therefore be described by a linear combination of the lattices

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \quad \text{where} \quad n_1, n_2, n_3 \in \mathbb{Z} \quad (1.103)$$

The set of independent lattices vectors $\{\vec{a}_i\}$ span a volume called a *unit cell*. This is the building block of the crystalline structure such that many identical units cells can be arranged together to fill the entire space. Since each $\{\vec{a}_i\}$ need not be orthogonal to each other or have same length, there are a plethora of possible unit cells that can be formed in nature. Fig. 1.5a shows three possible types of cubic unit cells that commonly occur in nature.

To represent a surface interacting with a solution, one usually chooses a single crystal plane of interest. A crystal plane is an infinite plane spanned by three non-colinear lattice points. It is usually denoted by a unique *Miller index*, a standard in crystallography, which is a set of three integers (hkl) that uniquely define its orientation. One can determine a Miller index by first calculating the intercept on the axes along the unit cell vectors in integer multiples of lattice constants, taking the inverses of those integers, and then reducing the ratio to three full integers. For example, the Miller index of the crystal plane represented in Fig. 1.5b is (233).

Why would one choose such an involved step to represent a lattice plane? The answer is related to the nature of the electrons confined to PBC. Using the inverse ratio of integer intercepts is not a rigorous definition but is rather a consequence — Miller index formally represents a set of coordinates for a vector in reciprocal space (k -space, or momentum-space) defined as the Fourier transform of position space. This vector is perpendicular to the lattice plane and therefore can uniquely define the crystal plane of interest. In addition, all possible lattice planes in a crystal structure can be represented in a Fourier transformed unit cell, known as the *First Brillouin Zone*. While k -space is an incredibly important concept for periodic electronic structure theory, it is rather peripheral from a practitioner's point of view modeling catalysis and therefore we do not further elaborate here. For a more rigorous presentation of solid state physics and periodic electronic

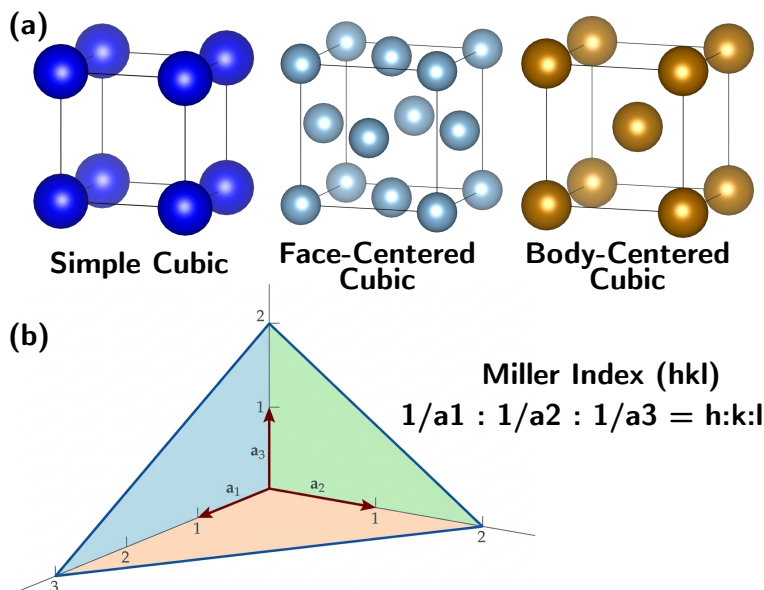


Figure 1.5: (a) A schematic of three commonly occurring cubic unit cells. From left to right: simple cubic, face-centered cubic (fcc), and body-centered cubic (bcc) unit cells. (b) A schematic of a sample crystal plane and its Miller index.

structure theory, we recommend interested readers to consult Refs. [212–216]. In particular, Ref. [216] offers a light but interesting perspective for readers more familiar with chemistry as it attempts to bridge physical chemistry concepts with solid state physics.

Finally, we elaborate the general procedure employed in this dissertation to design model *slabs*, a finite number of parallel atomic layers to model a surface. The first step is to optimize a conventional unit cell with a chosen level of theory. This can be performed through an optimization with variable lattice parameters, or many different single-point calculations with different lattice parameters, subsequently fitting the data points to interpolate lattice parameters that yield the lowest absolute energy. With the determined value, one constructs a *supercell* comprised of multiple unit cells. To capture the nature of the surface, a vacuum space of ≈ 20 Å is placed atop the facet of interest in the surface normal direction. This helps ensure that there is no fictitious interaction between the two images along the surface normal direction. Dipole corrections must be added in case the vacuum is not filled with a proper countercharge. [217] To verify if the final slab is an adequate model, the potential of zero charge (PZC) [218] is computed and compared with experimental values.

Implicit Model for Solvent and Electrolytes. In this dissertation, we mainly employ the Poisson-Boltzmann (PB) model as our choice of implicit description of the electrolyte solution. This model is the computational realization of the Gouy-Chapman model for EDL, [211, 219] incorporating a description of both the Helmholtz Layer and the diffuse layer. In addition, modifications to PB model can also be applied, such as incorporating Stern layer thickness. [210, 220, 221]

In a PB implicit solvation model, the solvent is represented as a dielectric medium with a diffuse cavity function that divides the solute and the solvent regions

$$\epsilon(\vec{r}) = 1 + (\epsilon_{\text{solvent}} - 1) \prod_{i=1}^{N_{\text{atoms}}} s_i^{\text{diel}}(d_i, \Delta, |\vec{r} - \vec{R}_i|) \quad (1.104)$$

where N_{atoms} is the number of atoms in the solute (i.e., quantum mechanical atoms), $\epsilon_{\text{solvent}}$ is the dielectric constant of the solvent (78.4 for H_2O), and 1 stands for vacuum permittivity. The cavity function s_i^{diel} employs an error function to change smoothly with position:

$$s_i^{\text{diel}}(d_i, \Delta, |\vec{r} - \vec{R}_i|) = \frac{1}{2} \left[1 + \text{erf} \left(\frac{|\vec{r} - \vec{R}_i| - d_i}{\Delta} \right) \right] \quad (1.105)$$

where d_i determines the center of the dividing surface, and Δ is the width of the rise from vacuum to $\epsilon_{\text{solvent}}$.

The implicit electrolyte is modeled as a distribution of point charges that follows Poisson-Boltzmann statistics. The corresponding charge density of ions $\rho_{\text{ion}}(\vec{r})$ will be

$$\rho_{\text{ion}}^{\text{PB}}(\vec{r}) = \sigma(\vec{r}) \sum_i^m q_i c_i \exp \left(-\frac{q_i \phi(\vec{r})}{k_{\text{B}} T} \right) \quad (1.106)$$

where ϕ is the total electrostatic potential of the system, q_i is the charge of the ion i , c_i is the concentration of the ion i , and $\sigma(\vec{r})$ is the dividing function

$$\sigma(d_\alpha, \Delta, |\vec{r} - \vec{R}|, a) = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{|\vec{r} - \vec{R}| - d_\alpha - a}{\Delta} \right) \right] \quad (1.107)$$

The form of σ is quite similar to Eq. (1.105) except for the additional constant a that places the center of the dividing surface further away from the origin of solute: a thus represents the effective Stern layer thickness controlled by the size of the counterion. In the limit of dilute concentrations of monovalent 1-to-1 electrolyte, we may Taylor expand Eq. (1.106) and incorporate only the leading term. This results in the *Linearized Poisson-Boltzmann* (LPB) equation

$$\rho_{\text{ion}}^{\text{LPB}}(\vec{r}) = \sigma(\vec{r}) \sum_i^m q_i c_i \left(1 - \frac{q_i \phi(\vec{r})}{k_B T} \right) \quad (1.108)$$

Finally, to account for the potential generated by both the ionic charge distribution and the dielectric, one computes the total electrostatic potential ϕ^{tot} generated by the solute-ion-dielectric system through the generalized Poisson equation

$$\vec{\nabla} \left[\epsilon(\vec{r}) + \vec{\nabla} \phi^{\text{tot}}(\vec{r}) \right] = -4\pi \left[\rho^{\text{sol}}(\vec{r}) + \rho^{\text{ions}}(\vec{r}) \right] \quad (1.109)$$

This is done by first computing the potential generated by the electron density, adding the potential generated by the nuclei (usually smeared out gaussian distributions), adding the potential generated from the ionic charge distribution (Eq. (1.106) or Eq. (1.108)) and solving Eq. (1.109). [19, 221–223] Once self-consistency is achieved, one may then add the additional electrostatic contribution to the energy. For the particular case of dilute, one-to-one electrolyte, we may employ the LPB equation and arrive at a special form of Eq. (1.109) which can be written as $\nabla^2 \phi^{\text{tot}} = \kappa^2 \phi^{\text{tot}}$ (also known as the Debye-Hückel form). This differential equation can be analytically solved, and is characterized by an ionic screening length $\lambda_D = \kappa^{-1}$ where

$$\lambda_D = \frac{1}{\kappa} = \left(\frac{\epsilon k_B T}{\sum_i^m q_i c_i} \right)^{1/2} \quad (1.110)$$

λ_D is also known as the *Debye length*.

Often, the defects of the implicit solvation model require the use of a hybrid implicit/explicit solvation model. These include the intercalation of the implicit electrolyte into internuclear regions and errors in the placement of the countercharge, which can lead to an erroneous prediction of the properties of the metal electrode. To ameliorate such shortcomings, hybrid implicit/explicit models are employed in this dissertation, in which the first solvation shell is treated with explicit solvent molecules.

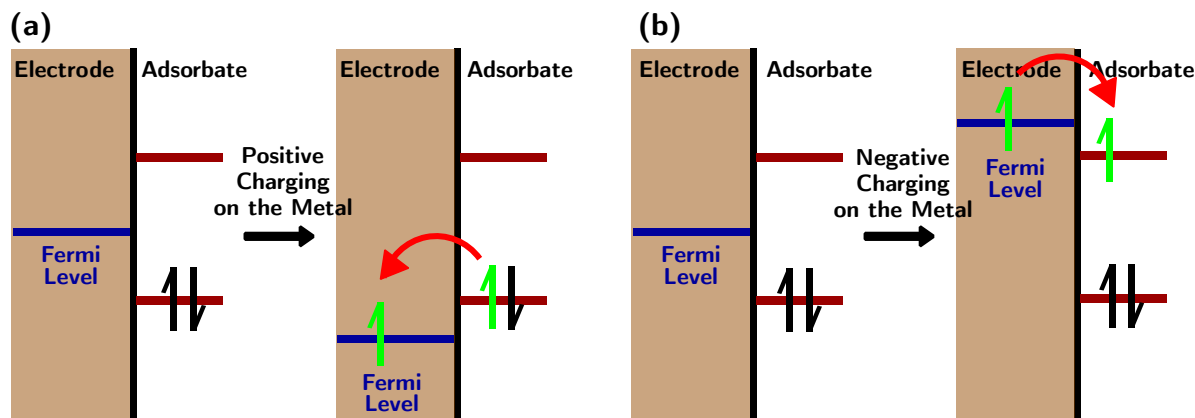


Figure 1.6: Schematic of the oxidation and reduction of adsorbate interaction with a metallic electrode. [224] (a) Schematic of the oxidation of the adsorbate. When the Fermi level (blue bar) is pushed below LUMO of the adsorbate (brown bars), an electron can migrate from and the adsorbate. (b) Schematic of the reduction of the adsorbate. When the Fermi level (blue bar) rises above the HOMO of the adsorbate (brown bars), an electron can migrate to the adsorbate.

1.4.3 Modeling Electrode Potential with DFT

Including the effect of the applied of potential on a metal electrode is critical for modeling electrochemical processes. Fig. 1.6 provides a simplified schematic illustrating how a molecule adsorbed to a surface can be oxidized or reduced through a change of applied potential. [224] The left panel of Fig. 1.6a represents an open circuit condition. The Fermi level — the HOMO equivalent for metals — of the electrode is located between the HOMO and LUMO of the adsorbate. Positive charging on the metal (e.g., via an anodic current) will lower the Fermi level of the metal. Once the Fermi level is placed below the HOMO of the adsorbate, the electron can hop from the HOMO of the adsorbate to the Fermi level of the metal, resulting in the oxidation of the adsorbate species. The opposite scenario is also possible and is shown in Fig. 1.6b. In this case, the negative charging (e.g., via a cathodic current) will increase the Fermi level of the metal, allowing the electrons within the metal to transfer to the LUMO and reduce the adsorbate. Therefore, an effective modeling of the applied potential is highly important for electrochemical heterogeneous catalysis.

The Computational Hydrogen Electrode (CHE). Perhaps the first widely used approach in modeling electrode potential was developed by Nørskov and co-workers in 2004, [11] the approach that was later termed as the Computational Hydrogen Electrode (CHE) model. [225–227] CHE is simple but still widely used to capture the thermodynamics of electrochemical reactions by introducing a secondary reaction. Let us consider a key reaction that occurs at the electrode: the Hydrogen Evolution Reaction (HER). [228–230] HER is the main proton source for almost all catalytic intermediates and products. It is also the main side reaction that competes with or dominates over the main reaction of interest. In acidic conditions, HER is a two-electron process,

combining two protons to produce hydrogen gas



HER is known to proceed through the Volmer-Heyrovsky-Tafel mechanism. [230–232] The first step is the Volmer reaction (Eq. (1.112))



Here the asterisk (*) indicates the electrode. The second step is either the Tafel (Eq. (1.113)) or the Heyrovsky (Eq. (1.114)) reaction



The Tafel step would be preceded by an additional Volmer step to prepare another $* \text{H}$. All of these reactions depend on the free energy of the proton-electron pair that which depends on the applied potential U . Instead of computing this, one may instead calculate the free energy change of the following thermal process



and add it to the equilibrium coupling between $(\text{H}^+ + \text{e}^-)$ and $\text{H}_2 (\text{g})$



Eq. (1.116) is precisely the definition of the *Reversible Hydrogen Electrode* (RHE), one of the reference reactions used to measure applied potentials. The reactant and products are at equilibrium when the applied bias is 0.0 V vs. RHE, and the changes in free energy can be modeled through required differential electric work. For example, the free energy change of the Volmer step is

$$\Delta G_{\text{Volmer}}(U) = \Delta G_{\text{H}} + eU_{\text{RHE}} \quad (1.117)$$

where U_{RHE} is the applied potential measured with respect to RHE and ΔG_{H} is the potential-independent thermal free energy change of Eq. (1.115). The CHE can be applied to other reactions that involve protons in their catalytic mechanisms and indeed has been the workhorse method of much computational electrocatalysis work. [227] In addition, the reference reaction (Eq. (1.116)) may also be chosen to be another reaction to better fit the electrochemistry of interest. [227] The CHE can also be used with fully explicit description of the solution/electrode with proper consideration of charge neutrality. This approach however must come with careful, rigorous, and thus computationally demanding conformational sampling strategies search and sample the global/local minima of the hyper-dimensional PES. [233, 234]

Constant Electrode Potential (CEP) Model:

Vary the number of electrons in simulation cell
such that the Fermi level (and thus, the potential) remains constant.

U : Electrode potential ϵ_F : Fermi Level
 e : elementary charge
 ϕ_{ref} : Work function of the reference electrode

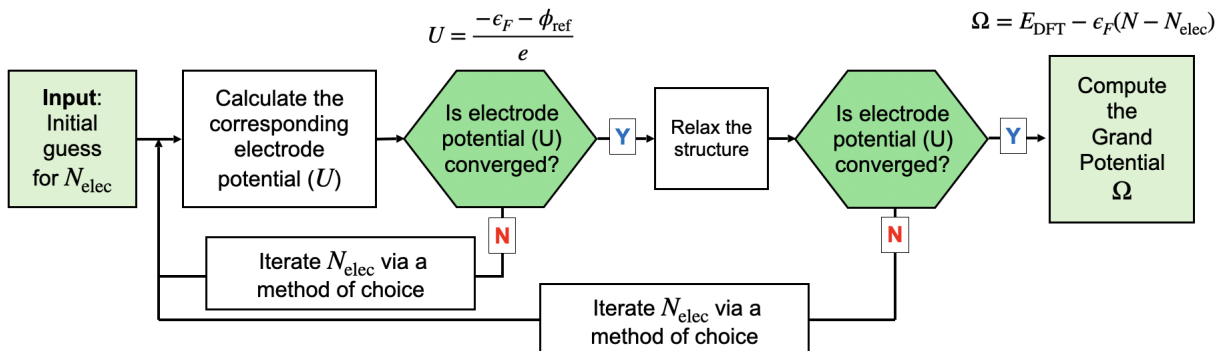


Figure 1.7: The computational workflow of the Constant Electrode Potential model. This dissertation primarily uses Newton’s secant method to optimize the number of electrons N_{elec} .

Self-consistent Modeling of the Electrode Potential. While the CHE is a useful model in terms of simple thermodynamics, it effectively adds an electric work correction to the energy computed through a single DFT calculation after a geometry optimization is converged without bias. Therefore, it does not self-consistently include the effect of the applied electrode potential on the structure and conformations of adsorbates as well as nearby solvent/electrolyte structure.

One strategy to go beyond CHE is the *Constant Electrode Potential* framework (CEP). [235] The key takeaway from Fig. 1.6 is that the Fermi level of the metallic electrode is correlated with the potential applied to the system. In fact, the measured electrode potential U with respect to some reference electrode is linearly related

$$U = \frac{-\epsilon_F - \phi_{\text{ref}}}{e} \quad (1.118)$$

where ϕ_{ref} is the absolute work function of the reference electrode. Therefore, one may instead set up an electron reservoir to allow variation of the number of electrons N_{elec} with changes in the Fermi level. The CEP framework achieves this by optimizing both N_{elec} and the atomic forces via a doubly nested self-consistent loop (Fig. 1.7). This structure ensures that both N_{elec} and the atomic forces are converged to a desired value. This workflow has been applied to various electrocatalysis reactions such as electrochemical reduction of carbon dioxide. [236–238]

A couple of important features that this workflow must accommodate are noted. First, the CEP-DFT must include a proper countercharge (either via a homogeneous background [239–241] or via an implicit PB/LPB solvation model). This is critical as CEP-DFT inherently allows the number of electrons to deviate from neutral, which may cause divergent behavior without a proper countercharge. In addition, CEP-DFT must allow fractional (i.e., non-integer) number of electrons. Additional theoretical details can be found in Appendix A.

Grand-canonical DFT. The workflow described above is driven by the fixed chemical potential associated with the applied bias, which allows the number of electrons within the system to vary (i.e., *grand-canonical* in the electrons). Another alternative is therefore a theory that optimizes the wavefunction or density defined by independent variables suitable for systems under applied bias. Using the language of statistical mechanics, a theory of open quantum systems whose independent variables are chemical potential μ , temperature T , and volume V can be a rigorous approach (i.e., a quantum system in a *grand canonical ensemble*). In fact, there has been a surge of interest in research of grand-canonical analogues of HF and DFT in the literature. These include approaches that minimize the grand potential with respect to a fixed chemical potential using a Lagrange multiplier method [242] or introducing an auxiliary matrix quantity to perform unconstrained minimization of a grand-canonical DFT functional. [243] We direct interested readers to Refs [242–248].

1.5 Outline of the Dissertation

The remaining chapters of this thesis aim to apply single-reference theories in modeling various aspects of heterogeneous catalysis. In Chapter 2, highly accurate core-electron binding energies measured by X-ray Photoelectron Spectroscopy (XPS) are modeled and computed with OO-DFT and relativistic effects. In Chapters 3 and 4, various elementary steps of ion-transfer reactions (e.g., corrosion and deposition) that can significantly affect the durability of catalytic devices are modeled using CEP-DFT. A brief synopsis of each chapter follows:

Chapter 2. The contents of this chapter are adapted with permission from the authors of the following article: **Kang, R***; Cunha, L. A.*; Hait, D.; Head-Gordon, M. "Extending Orbital-Optimized Density Functional Theory to L-Edge XPS and Beyond: Spin–Orbit Coupling via Nonorthogonal Quasi-Degenerate Perturbation Theory," *J. Chem. Theory Comput.*, 21 (17), 8391–8405, 2025. (* indicates equal contribution from authors.)

Abstract: Quantum mechanical calculations of core electron binding energies (CEBEs) are relevant to interpreting x-ray photo-electron spectroscopy (XPS). Orbital-optimized density functional theory (OO-DFT) accurately predicts K-edge CEBEs but is challenged by the presence of significant spin-orbit coupling (SOC) at L- and higher edges involving inner-shell orbitals with nonzero angular momentum. To extend OO-DFT to L-edges and higher, our method utilizes scalar-relativistic, spin-restricted open-shell OO-DFT to construct a minimal, quasi-degenerate basis of core-hole states corresponding to a chosen inner-shell (e.g. ionizing all six possible 2p spin orbitals). Non-orthogonal configuration interaction (NOCI) is then used to obtain the matrix elements of the full Hamiltonian including SOC in this quasi-degenerate model space of determinants. Using a screened 1-electron SOC operator parametrized with the Dirac-Coulomb-Breit (DCB) Hamiltonian results in doublet splitting (DS) values for 3rd row elements that are nearly in quantitative agreement with experiment. The resulting NOCI eigenvalues are shifted by the average of the (scalar) OO-DFT CEBEs to yield CEBEs (split by SOC) corrected for dynamic correlation. Comparing

calculations on gas phase molecules with experimental results establishes that NO-QDPT with the SCAN functional (NO-QDPT/SCAN), using the DCB screened 1-electron SOC operator is accurate to about 0.2 eV for L-edge CEBEs of molecules containing 3rd row atoms. However, this NO-QDPT approach becomes less accurate for 4th-row elements starting in the middle of the 3d transition metal series, with errors increasing as atomic number increases.

Chapter 3. The contents of this chapter are adapted with permission from the authors of the following article: **Kang, R.**; Zhao, Y.; Hait, D.; Gauthier, J. A.; Kempler, P. A.; Thurman, K. A.; Boettcher, S. W.; Head-Gordon, M. "Understanding ion-transfer reactions in silver electrodis-solution and electrodeposition from first-principles calculations and experiments," *Chem. Sci.*, 15, 4996-5008, 2024.

Abstract: The electrified aqueous/metal interface is critical in controlling the performance of energy conversion and storage devices, but an atomistic understanding of even basic interfacial electrochemical reactions challenges both experiment and computation. We report a computational study of (reversible) ion-transfer reactions involved in anodic Ag corrosion/deposition, a model system for interfacial electrochemical processes generating or consuming ions. With the explicit modeling of the electrode potential and a hybrid implicit–explicit solvation model, the density functional theory calculations produce free energy curves predicting thermodynamics, kinetics, partial charge profiles, and reaction trajectories. The calculated (equilibrium) free energy barriers (0.2 eV), and their asymmetries, agree with experimental activation energies (0.4 eV) and transfer coefficients, which were extracted from temperature-dependent voltage-step experiments on Au-supported, Ag-nanocluster substrates. The results indicate that the barrier is controlled by the bias-dependent competition between partial solvation of the incipient ion, metal–metal bonding, and electrostatic stabilization by image charge, with the latter two factors weakened by stronger positive biases. We also report simulations of the bias-dependence of defect generation relevant to nucleating corrosion by removing an atom from a perfect Ag(100) surface, which is predicted to occur via a vacancy-adatom intermediate. Together, these experiments and calculations provide the first validated, accurate, molecular model of the central steps that govern the rates of important dissolution/deposition reactions broadly relevant across the energy sciences.

Chapter 4.

Abstract: Understanding changes and degradation of the copper cathode during the electrochemical carbon dioxide reduction reaction (CO₂RR) is a fundamental challenge. Advances in *operando* experimental methods and computational tools have shed light on the degradation mechanisms. However, the role of the hydroxide ions formed from the alkaline Volmer reaction remains under-studied. Here we report a computational investigation of Cu(OH)_n adatom complexes that can form on a roughened surface as possible intermediates that can lead to cathodic copper corrosion. Series of constant-potential density functional theory calculations are utilized to compute the voltage-dependent free energy surfaces of Cu(OH)_n electrodis-solution from adatom defects on a Cu(100) surface. The results show that the dissolution of a Cu(OH) adatom complex is endergonic by

~ 1 eV at an electrode bias of -1.59 V vs. the Standard Hydrogen Electrode (SHE) and thus quite unfavorable. In contrast, the dissolution of $[\text{Cu}(\text{OH})_2]^-$ at the same bias only requires ~ 0.2 eV. The Cu oxidation states of both complexes are +1 regardless of the applied potential. The atomic partial charges and their change show that hydroxides of surface-bound $^*\text{Cu}(\text{OH})_2$ induce an image quadrupole which allows facile dissociation. Pathways to form these two complexes are analyzed using transition state calculations evaluated at constant potential. The presence of oxygen adatoms, for example from subsurface oxygen, is identified to facilitate the formation of $\text{Cu}(\text{OH})_n$ via dissociative chemisorption of water. The results show that hydroxide-ion mediated cathodic Cu dissolution is viable. Remaining questions and further work that could validate the proposed mechanism are discussed.

Chapter 2

Extending Orbital-Optimized Density Functional Theory to L-edge XPS and Beyond

2.1 Introduction

X-ray photoelectron spectroscopy (XPS) is a widely used analytical technique in the physical sciences.[249, 250] It dates back to the 1970s when Kai Siegbahn and Ulrik Gelius pioneered electron spectroscopy for chemical analysis (ESCA) which enabled the determination of core-electron binding energies of free molecules (and condensed matter).[251–256] ESCA yielded crucial insights into core-ionization processes such as resonances, core-hole lifetimes, and gas-phase shake-up peaks, leading to Siegbahn sharing the 1981 Physics Nobel Prize “for his contribution to the development of high-resolution electron spectroscopy.” Today, XPS (the modern name for ESCA[257]) remains widely used for investigating condensed matter and interfacial phenomena.[258] Some examples of its application include characterization of carbon-based materials[259, 260], energy storage devices, [261–263] photoactive materials[264, 265] and bio-organic materials[266].

The value of XPS stems from the element and shell specificity of the core-electron binding energies (CEBEs), which usually lie in a relatively narrow characteristic range. The precise location of the signals within this range reflects the local environment of each atom, such as oxidation state or the nature of chemical bonding.[250, 267] Therefore reliable measurements of CEBEs provide key analytical information,[268] whose interpretation can be greatly aided by *ab initio* CEBE calculations. We note that different sets of experimental CEBEs are subject to calibration errors[258, 269] that have entered XPS electron binding energy data banks.[269]

The most widely used approaches for XPS calculations on molecules and condensed phase systems are computationally inexpensive ones based on density functional theory (DFT).[76, 77, 270] The simplest approach is the direct use of ground-state orbital energies in a Koopman-like manner, but this typically yields very large errors with standard functionals.[271] Functionals with reduced self-interaction, however, lead to improved results.[272, 273] There are two commonly

used alternatives. First is the well-established Δ -SCF method[176–178, 274–281] which captures key orbital relaxation effects (also referred to as orbital-optimized (OO)-DFT, particularly when generalized to excitations[164]). With the aid of special solvers[169–171, 178] to converge to high-order saddle points in orbital space, OO-DFT methods predict highly accurate K-edge XPS (and X-ray absorption) spectra even for early transition metals,[194] upon inclusion of scalar relativistic effects. Extensions of the OO approach to coupled cluster methods for K-shell CEBEs yield even higher accuracy.[282, 283] The second category of methods are based on Slater’s transition state method,[284] suitably generalized.[285–287] Developments in this direction also continue.[288–290]

In contrast to the K-edge features arising from ionization of 1s electrons, spin-orbit coupling (SOC) effects challenge calculations of core-ionized states from levels with non-zero angular momenta. For example, the 2p energy levels are split into $j = 3/2$ and $j = 1/2$ components by SOC according to how the unpaired electron spin 1/2 couples to its orbital angular momentum of 1. Ionization from 2p levels therefore leads to two distinct peaks in the XPS spectrum, generally labeled as the lower energy L_3 (ionization out of $j = 3/2$) and higher energy L_2 (ionization out of $j = 1/2$) features. The separation of the two peaks is called doublet splitting (DS), which is another element-specific spectral signature from XPS.

There have been relatively few reports of DFT calculations on 2p CEBEs.[177, 291–293] While one may use experimental DS values to model molecular L-edge spectra,[177, 294, 295] *ab initio* approaches that include SOC for L-edges are still an area of active research. Notably, nonrelativistic equation-of-motion coupled cluster single and doubles (EOM-CCSD) has been used to generate the set of relevant states, which were mixed under the Breit-Pauli SOC Hamiltonian to obtain L-edge spectra.[296, 297] However, EOM-CCSD misses the orbital relaxation effects that make OO-DFT so successful for K-edges. On the other hand, non-orthogonal configuration interaction (NOCI)[182, 183, 188, 298, 299] has been proposed as an alternative approach to couple relaxed orbital core-ionized configurations to compute L-edge XAS.[300] While the main spectral features were present, the accuracy of that approach is limited by the lack of dynamic correlation.

Extending the success of OO-DFT for K-edges to L-edges and beyond is therefore an open challenge, with the key question being how to capture SOC, dynamic electron correlation and orbital relaxation together. In this work, we propose a solution towards that objective by combining OO-DFT and NOCI with a treatment of SOC via the exact 2-component (X2C)[204, 205, 301–303] model. The resulting method has the advantage of addressing all three factors that are important for accurate L-edge calculations, as well as only requiring moderate computational effort. While our proposed approach is not fully *ab initio*, highly encouraging results are obtained for calculations of L-edge energies and their DS values for molecules composed of main-group elements and transition-metal complexes. For example, the root mean squared error (RMSE) of DS and CEBE predictions are just 0.04 eV and 0.2 eV respectively for L-edges in molecules containing third-row main-group elements, vs experiment.

The remainder of this paper is organized as follows. First we present an overview of the theory underlying our computational framework (Section 2.2), followed by a discussion of the main results in Section 2.3, which include validation of the method for valence SOC splitting, and benchmarks across a range of molecules for 2p core-ionizations. We also explore the performance for extreme

ultraviolet (XUV) accessible ionizations from M (3p and 3d) and N (4d) edges of a few heavier elements. We conclude in Section 2.4 with a summary and future outlook.

2.2 Theory and Implementation

2.2.1 One-Electron Exact Two Component Theory (1eX2C)

One-electron exact two-component (1eX2C) theory decouples the large and small components of the four-component Dirac Hamiltonian. [204, 205, 301, 302] We direct interested readers to Refs [195, 196, 303, 304] for further details and only provide a brief outline here. The 1eX2C approach is based on the one-electron operator $\hat{W} = (\hat{\vec{\sigma}} \cdot \hat{\vec{p}})\hat{V}(\hat{\vec{\sigma}} \cdot \hat{\vec{p}})$, where $\hat{p}$ is the electron momentum, $\hat{V}$ is the nuclear attraction, and $\hat{\vec{\sigma}}$ the vector of the Pauli operators. The use of a finite atom-centered basis reduces the single-particle Dirac equation in the restricted kinetic balance form [305] to the following eigenproblem:

$$\begin{bmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & \frac{\mathbf{W}}{4c^2} - \mathbf{T} \end{bmatrix} \begin{bmatrix} \mathbf{C}_L \\ \mathbf{C}_S \end{bmatrix} = \epsilon \begin{bmatrix} \mathbf{S} & 0 \\ 0 & \frac{1}{2c^2} \mathbf{T} \end{bmatrix} \begin{bmatrix} \mathbf{C}_L \\ \mathbf{C}_S \end{bmatrix} \quad (2.1)$$

where $\mathbf{T}$, $\mathbf{V}$, and $\mathbf{W}$ are the atomic orbital (AO) basis matrix representations of the operators for nonrelativistic kinetic energy ($\hat{T}$), $\hat{V}$, and $\hat{W}$. $\mathbf{S}$ is the overlap matrix between the AO basis functions, $\mathbf{C}_L$ is the large component and $\mathbf{C}_S$ the small component.

It is straightforward to decompose $\hat{W}$ into spin-free $\hat{W}^{\text{SF}}$ and spin-orbit $\hat{W}^{\text{SO}}$ parts, via:

$$\hat{W} = (\hat{\vec{\sigma}} \cdot \hat{\vec{p}})\hat{V}(\hat{\vec{\sigma}} \cdot \hat{\vec{p}}) = \left(\hat{\vec{p}} \cdot \hat{V} \hat{\vec{p}} + i \hat{\vec{\sigma}} \cdot (\hat{\vec{p}} \times \hat{V} \hat{\vec{p}}) \right) \equiv \hat{W}^{\text{SF}} + i \hat{\vec{\sigma}} \cdot \hat{W}^{\text{SO}} \quad (2.2)$$

$\hat{W}^{\text{SF}}$ is spin-independent and leads to scalar relativistic effects. On the other hand, the $i \hat{\vec{\sigma}} \cdot \hat{W}^{\text{SO}}$ term is spin-dependent and does not commute with spin-operators. It thus couples different spin-states, leading to spin-orbit phenomena.

Decoupling the large and small components of the Dirac Hamiltonian (Eq. (2.1)) and writing it in a block-diagonal form requires defining the following transformations [196]:

$$\mathbf{X} = \mathbf{C}_S (\mathbf{C}_L)^{-1} \quad (2.3)$$

$$\tilde{\mathbf{S}} = \mathbf{S} + \frac{1}{2c^2} \mathbf{X}^\dagger \mathbf{T} \mathbf{X} \quad (2.4)$$

$$\mathbf{R} = \mathbf{S}^{-1/2} \left(\mathbf{S}^{-1/2} \tilde{\mathbf{S}} \mathbf{S}^{-1/2} \right)^{-1/2} \mathbf{S}^{1/2} \quad (2.5)$$

which can be used to define the relativistic one-electron Hamiltonian matrix $\mathbf{h}_1^{\text{X2C}} = \mathbf{T}^{\text{X2C}} + \mathbf{V}^{\text{X2C}}$ in terms of the effective kinetic energy $\mathbf{T}^{\text{X2C}}$ and nuclear attraction $\mathbf{V}^{\text{X2C}}$ terms:

$$\mathbf{T}^{\text{X2C}} = \mathbf{R}^\dagger \left(\mathbf{T} \mathbf{X} + \mathbf{X}^\dagger \mathbf{T} - \mathbf{X}^\dagger \mathbf{T} \mathbf{X} \right) \mathbf{R} \quad (2.6)$$

$$\mathbf{V}^{\text{X2C}} = \mathbf{R}^\dagger \left(\mathbf{V} + \frac{1}{4c^2} \mathbf{X}^\dagger \mathbf{W} \mathbf{X} \right) \mathbf{R} \quad (2.7)$$

We may also carry out the procedure described by Eqs. (2.3)-(2.7) with only the spin-free part of $\hat{W}$ (i.e., explicitly replacing $\mathbf{W}$ in Eqn. (2.1) and subsequent steps with $\mathbf{W}^{\text{SF}}$), to define a scalar-relativistic one-electron Hamiltonian matrix $\mathbf{h}_1^{\text{SF-X2C}} = \mathbf{T}^{\text{SF-X2C}} + \mathbf{V}^{\text{SF-X2C}}$. We note that $\mathbf{T}^{\text{SF-X2C}}$ and $\mathbf{V}^{\text{SF-X2C}}$ differ from $\mathbf{T}^{\text{X2C}}$ and $\mathbf{V}^{\text{X2C}}$ as explicitly defined in Eqs. (2.6)-(2.7). This is due to the dependence of the transformation matrices $\mathbf{X}$, $\tilde{\mathbf{S}}$, and $\mathbf{R}$ on the nature of $\mathbf{W}$, i.e. whether only the spin-free term is used or the full operator.

With inclusion of the nonrelativistic electron-electron repulsion $\hat{G}^{\text{NR}}$ and the scalar nuclear-nuclear repulsion term V_{nn} , we can define the full 1eX2C and SF-1eX2C Born-Oppenheimer molecular Hamiltonians $\hat{H}^{\text{1eX2C}}$ and $\hat{H}^{\text{SF-1eX2C}}$ to be:

$$\hat{H}^{\text{1eX2C}} = \hat{h}_1^{\text{X2C}} + \hat{G}^{\text{NR}} + V_{nn} = \hat{T}^{\text{X2C}} + \hat{V}^{\text{X2C}} + \hat{G}^{\text{NR}} + V_{nn} \quad (2.8)$$

$$\hat{H}^{\text{SF-1eX2C}} = \hat{h}_1^{\text{SF-X2C}} + \hat{G}^{\text{NR}} + V_{nn} = \hat{T}^{\text{SF-X2C}} + \hat{V}^{\text{SF-X2C}} + \hat{G}^{\text{NR}} + V_{nn} \quad (2.9)$$

The spin-orbit contribution in 1eX2C is therefore:

$$\hat{h}_1^{\text{SOC-X2C}} = \hat{H}^{\text{1eX2C}} - \hat{H}^{\text{SF-1eX2C}} \equiv \hat{h}_1^{\text{X2C}} - \hat{h}_1^{\text{SF-X2C}} \quad (2.10)$$

without any two-electron contribution. Exact two-component theory can also include two-electron terms, but their implementation is not straightforward (for discussion and alternatives, see Refs [306–308]). Using only spin-free one-electron terms also permits direct use of DFT exchange-correlation (XC) functionals [194, 309], as XC functionals do not depend on the one-electron Hamiltonian. However, the presence of spin-orbit terms requires (non-standard) non-collinear density functionals.[310–313]

A simpler (but not *ab initio*) approach to partially account for two-electron SOC effects stemmed from the observation that they screen the one-electron terms,[314] which motivated empirical tuning of the one-body SOC contribution $\mathbf{h}_1^{\text{SOC-X2C}}$. The Screened-Nuclear-Spin-Orbit (SNSO) approximation [314], and subsequent modifications [315, 316] scale the matrix elements based on the angular momentum of the basis,

$$\mathbf{h}_1^{\text{SOC-SNSO}} \equiv \mathbf{h}_1^{\text{SOC-X2C}} - \mathbf{Q}\mathbf{h}_1^{\text{SOC-X2C}}\mathbf{Q} \quad (2.11)$$

$$\mathbf{h}_1^{\text{X2C-SNSO}} \equiv \mathbf{h}_1^{\text{SF-X2C}} + \mathbf{h}_1^{\text{SOC-SNSO}} \quad (2.12)$$

where $\mathbf{Q}$ is a diagonal matrix of angular-momentum-dependent coefficients. New SNSO coefficients based on four-component Dirac-Coulomb-Breit (DCB) Hamiltonian orbital splitting results are available in two forms[317]: either universal (DCB-SNSO) or dependent on the row of the periodic table (rDCB-SNSO). In this work, we apply SNSO via Eq. (2.12), although scaling $\mathbf{W}_{SO}$ (and not $\mathbf{h}_1^{\text{SOC-X2C}}$) has also been used elsewhere in the literature. [315, 316, 318] An alternative is to use empirical effective nuclear charge scaling, Z_{eff} , in the electron-nuclear attraction term. [319–321] We describe the use of Z_{eff} charges to compute the one-body model X2C operator $\hat{h}_1^{\text{X2C-}Z_{\text{eff}}}(Z_{\text{eff}})$ in Sec. B.1. Both the SNSO and the Z_{eff} approaches lead to many-body X2C model relativistic Hamiltonians of the form:

$$\hat{h}_1^{\text{X2C-model}} = \hat{h}_1^{\text{SF-X2C}} + \hat{h}_1^{\text{SOC-model}} \quad (2.13)$$

$$\hat{H}^{\text{1eX2C-model}} \equiv \hat{h}_1^{\text{X2C-model}} + \hat{G}^{\text{NR}} + V_{nn} \quad (2.14)$$

Operator	Description
Fundamental Operators	
$\hat{V}$	Nonrelativistic nuclear attraction potential.
$\hat{T}$	Nonrelativistic kinetic energy.
$\hat{G}^{\text{NR}}$	Nonrelativistic electron-electron repulsion.
V_{nn}	Nonrelativistic nuclear-nuclear repulsion (scalar).
$\hat{W} = (\hat{\sigma} \cdot \hat{p})\hat{V}(\hat{\sigma} \cdot \hat{p})$	One-electron operator central to 1eX2C.
$\hat{W}^{\text{SF}} = \hat{p} \cdot \hat{V} \hat{p}$	Scalar relativistic component of $\hat{W}$.
$\hat{W}^{\text{SO}} = i\hat{\sigma} \cdot (\hat{p} \times \hat{V} \hat{p})$	Spin-orbit component of $\hat{W}$.
One-electron Hamiltonians for X2C	
$\hat{h}_1^{\text{X2C}}$	One-electron X2C Hamiltonian.
$\hat{h}_1^{\text{SF-X2C}}$	Scalar-relativistic one-electron X2C Hamiltonian.
$\hat{h}_1^{\text{SOC-X2C}} = \hat{h}_1^{\text{X2C}} - \hat{h}_1^{\text{SF-X2C}}$	Spin-orbit contribution to the one-electron X2C Hamiltonian.
$\hat{h}_1^{\text{X2C-model}} = \hat{h}_1^{\text{SF-X2C}} + \hat{h}_1^{\text{SOC-model}}$	One-electron X2C Hamiltonian including a model spin-orbit term.
$\hat{h}_1^{\text{X2C-SNSO}} = \hat{h}_1^{\text{SF-X2C}} + \hat{h}_1^{\text{SOC-SNSO}}$	One-electron X2C Hamiltonian including a SNSO-screened SOC term.
$\hat{h}_1^{\text{X2C-Zeff}} = \hat{h}_1^{\text{SF-X2C}} + \hat{h}_1^{\text{SOC-Zeff}}$	One-electron X2C Hamiltonian including a Z_{eff} -screened SOC term.
Born–Oppenheimer molecular Hamiltonians	
$\hat{H}^{\text{1eX2C}} = \hat{h}_1^{\text{X2C}} + \hat{G}^{\text{NR}} + V_{nn}$	Molecular Hamiltonian within the 1eX2C framework.
$\hat{H}^{\text{SF-1eX2C}} = \hat{h}_1^{\text{SF-X2C}} + \hat{G}^{\text{NR}} + V_{nn}$	Molecular Hamiltonian within SF-1eX2C.
$\hat{H}^{\text{1eX2C-model}} = \hat{h}_1^{\text{X2C-model}} + \hat{G}^{\text{NR}} + V_{nn}$	Molecular Hamiltonian for a spin-orbit model (e.g., SNSO or Z_{eff}) based on 1eX2C.

Table 2.1: Summary of key operators.

A summary of key operators including the variants of one-electron Hamiltonians and the Born–Oppenheimer molecular Hamiltonians is provided in Table 2.1. Further details on the two-electron SOC terms as well as their approximations can be found in Refs [306–308, 322, 323].

2.2.2 Non-Orthogonal Treatment of Spin-Orbit Coupling

NOCI[187, 188, 298] diagonalizes the Hamiltonian within a subspace that is typically spanned by a set of individually optimized determinants that are hence not necessarily orthogonal to each other. This permits greater flexibility than traditional CI based on a single set of orthogonal orbitals. NOCI has been utilized to restore broken spatial symmetry[182, 298] and to simulate core-hole states[182–184, 298–300].

A fully variational treatment of SOC in our individual determinants is of course desired. However, $\hat{H}^{\text{1eX2C-model}}$ requires complex, spin-generalized orbitals. The scarcity of well-characterized non-collinear DFT functionals leaves Hartree-Fock (HF) as the most widely applicable spin-generalized mean-field approach available for orbital optimization with SOC. We will sidestep this limitation by performing orbital optimization at the scalar relativistic level for 2p ionization from a given atom and then subsequently incorporate SOC through the NOCI Hamiltonian. This seems justified because SOC is quite local in space (decaying as $\sim O(r^{-3})$), and the SOC interaction strength is much smaller than typical energy differences between different orbital subshells of a given atom. For example, the 2p subshell of Ar is ~ 250 eV below the continuum (and the energetically closest subshell is Ar 2s at ~ 330 eV), while the atomic DS is ~ 2 eV. We will therefore include SOC within the subspace of nearly degenerate states arising from local electron permutations within the relevant subshell: (e.g., the 6 core-hole states arising from 2p ionization on a given Ar atom). We shall refer to this formalism as Non-Orthogonal Quasi-Degenerate Perturbation Theory (NO-QDPT). We note that a similar rationale has been utilized in state-interaction based SOC treatments, such as in L-edge spectrum calculations in Ref. [324] utilizing SF-1eX2C EOM-CCSD states[325] and DFT/CIS L-edge calculations in Ref. [326] utilizing the Breit-Pauli Hamiltonian.

Given a ground state determinant $|\Psi_0\rangle$ and individually optimized core-hole determinants $|\Psi_1\rangle, |\Psi_2\rangle, \dots, |\Psi_N\rangle$, we compute the SOC effects through NOCI as follows:

1. Calculate overlap and Hamiltonian matrix elements within the core-hole state subspace:

$$H_{AB}^{\text{1eX2C-model}} = \langle \Psi_A | \hat{H}^{\text{1eX2C-model}} | \Psi_B \rangle \quad \text{where } A, B \in \{1 \dots N\} \quad (2.15)$$

$$S_{AB} = \langle \Psi_A | \Psi_B \rangle \quad \text{where } A, B \in \{1 \dots N\}. \quad (2.16)$$

2. Solve the generalized eigenvalue equation for core-hole states:

$$\mathbf{H}^{\text{1eX2C-model}} \mathbf{C}^{\text{1eX2C-model}} = E^{\text{1eX2C-model}} \mathbf{S} \mathbf{C}^{\text{1eX2C-model}} \quad (2.17)$$

to obtain the energies $\{E_i^{\text{1eX2C-model}}\}$ and states $\left\{ \sum_A C_{i,A}^{\text{1eX2C-model}} |\Psi_A\rangle \right\}, i \in \{1..N\}$. This procedure not only accounts for SOC, but also any splitting of inner-shell orbitals arising from non-spherically symmetric environments in molecular systems[327, 328].

3. Utilize the ground state energy $E_0^{\text{1eX2C-model}} = \langle \Psi_0 | \hat{H}^{\text{1eX2C-model}} | \Psi_0 \rangle$ to compute observable energy differences like inner-shell ionization energies etc.

This procedure is agnostic about *how* the determinants used in NOCI are obtained. The use of $|\Psi_0\rangle, |\Psi_1\rangle, |\Psi_2\rangle, \dots, |\Psi_N\rangle$ optimized with SF-1eX2C using HF defines NO-QDPT/HF: a wavefunction theory that incorporates SOC for core-hole state related observables but lacks dynamic electron correlation. In principle, however, it is possible to use any well-defined set of determinants, as we discuss next.

2.2.3 Shifting NOCI energies by OO-DFT

The formation of core-holes leads to a significant change in electron density, which can be effectively captured by direct optimization of orbitals for the core-hole state [177, 194, 274, 278, 329, 330]. Such optimizations have been hindered in the past by the risk of “variational collapse” to lower energy solutions, as core-hole states are seldom (if ever) minima of energy in orbital space. Recent efforts to develop reliable algorithms for optimizing saddle point solutions in DFT [169, 171, 178, 331–333] have been key to wider use of OO-DFT, with the SCAN[95] functional typically having an RMSE of ~ 0.3 eV vs experimental energies in the soft X-ray regime [176, 177, 194]. The larger errors obtained from OO-HF as compared to OO-DFT (*e.g.*, K-edge with SCAN[164]) indicate that it would be desirable to incorporate some dynamic correlation effects from suitable density functionals into prediction of inner-shell properties.

We therefore propose the following NO-QDPT/DFT scheme (also described in Fig. 2.1). It is a hybrid of the pure wavefunction approach and OO-DFT in which the multiplet *average* for a given subshell is obtained from OO-DFT and the subsequent spin-orbit splitting is obtained from wavefunction-based NOCI:

1. Use DFT calculations to obtain the ground state determinant $|\Psi_0\rangle$ and core-hole determinants $|\Psi_1\rangle, |\Psi_2\rangle, \dots, |\Psi_N\rangle$, via orbital optimization to extremize the energy functional corresponding to $\hat{H}^{\text{SF-1eX2C}}$. Let the resulting OO-DFT energies be $E_A^{\text{DFT;SF-1eX2C}}$ where $A \in \{0 \dots N\}$.
2. Evaluate the wavefunction theory (HF) energies of these determinants to obtain

$$E_A^{\text{HF;SF-1eX2C}} = \langle \Psi_A | \hat{H}^{\text{SF-1eX2C}} | \Psi_A \rangle \quad (2.18)$$

Then evaluate the shift for the ground state (ω_0) and the average shift for the core-hole state energies (ω_{CH}):

$$\omega_0 = E_0^{\text{DFT;SF-1eX2C}} - E_0^{\text{HF;SF-1eX2C}} \quad (2.19)$$

$$\omega_{\text{CH}} = \frac{1}{N} \sum_{A>0} \left(E_A^{\text{DFT;SF-1eX2C}} - E_A^{\text{HF;SF-1eX2C}} \right) \quad (2.20)$$

3. Calculate the overlap and Hamiltonian matrix elements within the core-hole state subspace from a wavefunction perspective:

$$H_{AB}^{\text{1eX2C-model}} = \langle \Psi_A | \hat{H}^{\text{1eX2C-model}} | \Psi_B \rangle \quad \text{where } A, B \in \{1 \dots N\} \quad (2.21)$$

$$S_{AB} = \langle \Psi_A | \Psi_B \rangle \quad \text{where } A, B \in \{1 \dots N\}. \quad (2.22)$$

4. Solve the generalized eigenvalue equation for core-hole wavefunctions:

$$\mathbf{H}^{\text{1eX2C-model}} \mathbf{C}^{\text{1eX2C-model}} = E^{\text{1eX2C-model}} \mathbf{S} \mathbf{C}^{\text{1eX2C-model}} \quad (2.23)$$

to obtain the NOCI energies $\{E_i^{\text{1eX2C-model}}\}$ and states $\left\{ \sum_A C_{i,A}^{\text{1eX2C-model}} |\Psi_A\rangle \right\}$

5. Obtain the ground state SOC containing wavefunction energy via:

$$E_0^{\text{1eX2C-model}} = \langle \Psi_0 | \hat{H}^{\text{1eX2C-model}} | \Psi_0 \rangle \quad (2.24)$$

6. Shift the SOC containing wavefunction energies via:

$$E_0 = E_0^{\text{1eX2C-model}} + \omega_0 = E_0^{\text{DFT;SF-1eX2C}} + \langle \Psi_0 | \hat{h}_1^{\text{SOC-model}} | \Psi_0 \rangle \quad (2.25)$$

$$E_i = E_i^{\text{1eX2C-model}} + \omega_{\text{CH}} \quad i \in \{1 \dots N\} \quad (2.26)$$

7. The core-ionization energies are thus $E_i - E_0$ etc. Note that the multiplet splittings $E_j - E_i = E_j^{\text{1eX2C-model}} - E_i^{\text{1eX2C-model}}$ ($i, j > 0$) are not affected by ω_{CH} (and hence are independent of DFT energies). Similarly, any splitting of inner-shell orbitals arising from a non-spherically symmetric molecular environment is unaffected by the average shift and is treated purely at the NOCI level. As a result, dynamic correlation effects are not accounted for in either the multiplet or molecular field splittings, but such contributions are expected to be quite small.[334]

2.2.4 Computational Details

The protocols described above were implemented in a development version of the Q-Chem package[335], which was used for all calculations. We used square gradient minimization (SGM[171]) to converge restricted open-shell (RO) core-ionized, orbital-optimized determinants. Use of RO orbitals avoids potential spin-contamination problems that may have downstream impacts on SOC inclusive NOCI calculations. DFT calculations used a radial grid with 99 points and an angular Lebedev grid with 590 points. A total of 8 mean-field methods for Slater determinant optimization were tested: HF, SCAN[95], SCAN hybridized with 10% HF exchange (SCANh), SCAN0[116], B3LYP[107], ω B97X-D3[336], ω B97X-V[337], and BHHLYP[338]. These functionals were chosen based on previous works which report the performance of OO-DFT for K-edges of main group elements.[164, 176, 177, 194]

As mentioned above, exploiting the locality of core orbitals and SOC, we utilize the one-center approximation to NOCI[183] for efficiency. The core-hole was thus localized onto a single atom for species with equivalent atoms (*e.g.*, Cl in CCl_4), which prevents errors arising from delocalization[106, 339] of the hole over multiple sites[177]. We did not separately optimize the α and β core-hole ionized states for closed-shell molecules – we simply obtain one and flip the spin of the unpaired electron to generate the other.

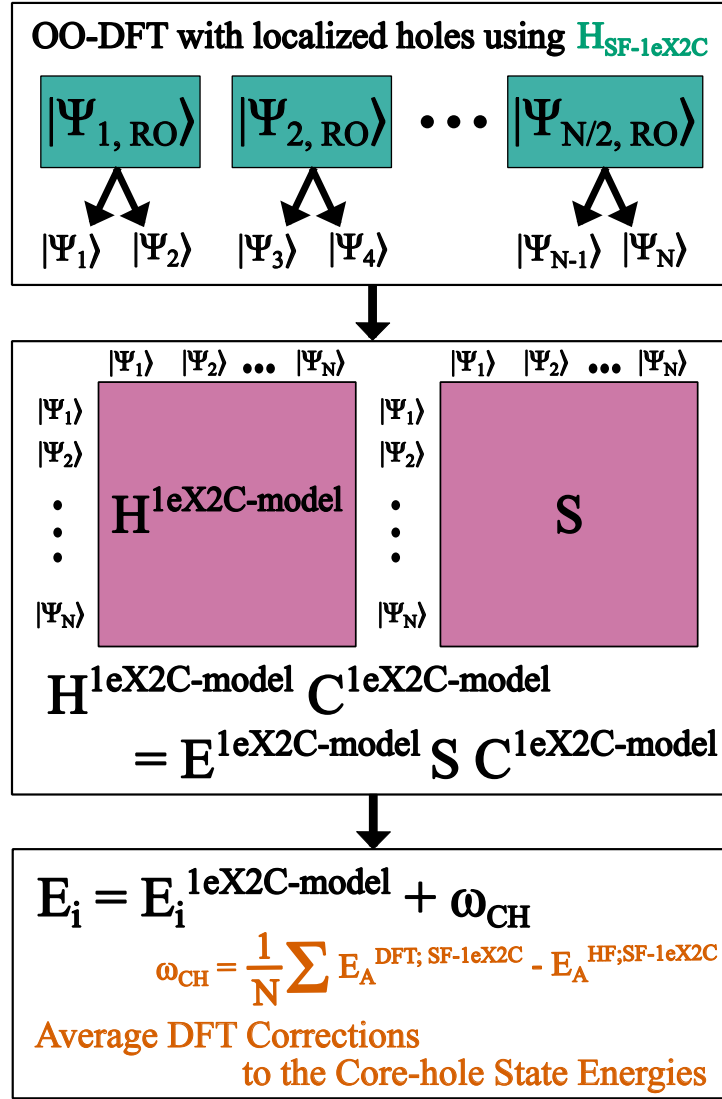


Figure 2.1: Flowchart for NO-QDPT using both OO-DFT and NOCI. (top) $N/2$ restricted open-shell (RO) OO-DFT calculations are performed using $\hat{H}^{\text{SF-1eX2C}}$. Spin-permutation is used to obtain two states from one ΔROHF . (center) NOCI eigenvalue problem is solved in the basis of N multi-electron states. (bottom) DFT corrections to the NOCI energies are applied to both ground state and core-hole states, although ground state correction is not described in the flowchart.

The open-shell core-hole determinants are pre-processed before spanning the $\hat{H}^{\text{1eX2C-model}}$ space. SOC induces mixing between spin-pure states, and the $N_{\text{AO}} \times N_{\text{AO}}$ real-valued coefficient/-density matrices from restricted open-shell optimizations have to be cast into $2N_{\text{AO}} \times 2N_{\text{AO}}$ sized matrices of complex numbers. A finite difference approach [194] to computing the $\mathbf{W}$ matrix elements was used for 1eX2C, for both the scalar-relativistic and spin-orbit parts. This scheme does not

produce significant errors compared to analytical approaches. [194] More details on computational aspects of NO-QDPT are available in Sec. B.2.

Gas phase experimental geometries from NIST CCCBDB[340] were used whenever possible. For molecules without experimental geometries, either MP2/cc-pVTZ structures from Ref. [177] were taken ($\text{P}(\text{CH}_3)_4$, $\text{Si}(\text{OCH}_3)_4$), or new structures were optimized using $\omega\text{B97M-V}$ [119]/def2-TZVPPD[341].

2.3 Results and Discussion

For brevity, henceforth we denote the 1eX2C based Born-Oppenheimer molecular Hamiltonians with particular screening models as:

- The unscreened 1eX2C Hamiltonian is denoted as X2C.
- The screened 1eX2C-DCB and 1eX2C-rDCB Hamiltonians are denoted as DCB-SNSO and rDCB-SNSO, respectively.
- The screened 1eX2C- Z_{eff} Hamiltonian is denoted as Z_{eff} .

2.3.1 Atomic Halogen Valence 2P State Splittings

To validate our approach and its implementation, we examined the valence splittings of atomic halogens. The ground state valence electronic configuration of the halogen atoms is ns^2np^5 (2P). SOC splits this sixfold degeneracy into $^2P_{3/2}$ and $^2P_{1/2}$ levels. Highly accurate experimental DS values are available, ranging from 404 cm^{-1} in F to 7603 cm^{-1} in I. Table 2.2 summarizes the errors (%) in calculated NO-QDPT DS, combined with X2C and the universal DCB-SNSO SOC parametrization.[317]. The lowest errors for each halogen atom are obtained from SCAN, SCANh, SCAN0, and $\omega\text{B97X-V}$ with DCB-SNSO, respectively, while unscreened SCAN/X2C leads to much larger errors. Results with the row dependent rDCB parameterization (rDCB) are similar to DCB. The value of the DFT-based NO-QDPT approach for the splittings is made clear by comparing DFT/DCB-SNSO errors against HF/DCB-SNSO errors. Comparing SCAN and HF, for instance, the HF errors are larger by factors of 3.5 (F) to 8 (Cl). In fact for all halogen atoms, the HF/DCB-SNSO errors are at least double that of the worst performing DFT functional. We reiterate that the NO-QDPT splittings arise purely through NOCI in the space of optimized determinants and are independent of DFT *energies*. Therefore, the improvement from HF to SCAN is solely the result of improved DFT *orbitals*. DFT orbitals also improve over HF in NO-QDPT predictions of alkali metal atom D-line splittings in Sec. B.4.

2.3.2 L_2 and L_3 Edges for 3rd Row Elements

We now explore the applicability of our NO-QDPT approach for computing the 2p CEBEs of 3rd row elements in gas phase molecules. NO-QDPT assumes that orbital relaxation in the presence of SOC is small. The validity of this assumption is tested via comparison to full ΔcGHF (*i.e.*, separate orbital optimization of $2p_{3/2}$ and $2p_{1/2}$ hole states with HF, in the presence of SOC) for four

		F	Cl	Br	I
Expt. (cm ⁻¹)		404	881	3685	7602
Method	Model ($\hat{H}$)	Error (%)			
HF	X2C	42.4	13.3	0.8	-4.5
SCAN	X2C	47.3	22.1	11.1	3.6
SCANh	X2C	46.8	21.4	10.2	3.1
SCAN0	X2C	46.1	20.2	8.8	2.3
B3LYP	X2C	47.4	23.9	11.0	3.7
ω B97X-D3	X2C	46.6	23.2	10.8	4.1
ω B97X-V	X2C	45.8	22.3	10.8	4.7
BHHLYP	X2C	45.8	20.4	7.6	1.2
HF	DCB-SNSO	-4.6	-6.5	-7.8	-9.8
SCAN	DCB-SNSO	-1.3	0.8	1.6	-2.2
SCANh	DCB-SNSO	-1.7	0.2	0.8	-2.7
SCAN0	DCB-SNSO	-2.1	-0.8	-0.4	-3.4
B3LYP	DCB-SNSO	-1.3	2.3	1.6	-2.1
ω B97X-D3	DCB-SNSO	-1.8	1.7	1.4	-1.7
ω B97X-V	DCB-SNSO	-2.3	0.9	1.4	-1.2
BHHLYP	DCB-SNSO	-2.3	-0.6	-1.5	-4.4

Table 2.2: Gas phase ground state halogen atom splittings calculated with NO-QDPT. Orbitals were computed using the decontracted aug-cc-p ω CVTZ [158, 160, 342, 343] (F, Cl) and decontracted aug-cc-p ω CVTZ-DK [344–348] (Br, I). The experimental values are obtained from NIST Atomic Spectra Database [349]. The experimental data is in wavenumbers (cm⁻¹) and the calculated errors are reported in percent (%). Experimental uncertainties in the reported values are 0.002 cm⁻¹ for F [350], <0.1 cm⁻¹ for Cl [351], 0.6655 cm⁻¹ for Br [352, 353] and 0.673 cm⁻¹ for I [354, 355].

simple hydrides and the Ar atom (Table 2.3). The computational details for converging Δ cGHF calculations are provided in Sec. B.3. The Koopman’s orbital energy model for the DS (*i.e.*, $\varepsilon(2p_{3/2}) - \varepsilon(2p_{1/2})$ for the neutral cGHF ground state) is also considered, as is NO-QDPT/SCAN. Similar to the behavior observed for ²P halogen atom valence splittings, Table 2.3 shows that X2C overestimates the L_{2,3}-edge DS values for all methods, with the errors growing with atomic number. By contrast, DCB-SNSO leads to much smaller errors (< 0.1 eV). The DCB-SNSO data for NO-QDPT/HF underestimates the DS by a nearly negligible 0.02-0.05 eV versus Δ cGHF, which validates its design. Interestingly, NO-QDPT/SCAN leads to a slightly lower difference with

		Ar	HCl	H ₂ S	PH ₃	SiH ₄
Expt. DS (eV)		2.15	1.63	1.20	0.90	0.60
		[356]	[357]	[358]	[359]	[360]
Method	Model ($\hat{H}$)	Error (eV)				
Koopman cGHF	X2C	0.49	0.4	0.33	0.23	0.21
Δ SCF cGHF	X2C	0.43	0.35	0.29	0.19	0.19
NO-QDPT HF	X2C	0.37	0.30	0.25	0.17	0.16
NO-QDPT SCAN	X2C	0.42	0.34	0.28	0.19	0.18
NO-QDPT SCAN0	X2C	0.41	0.33	0.27	0.18	0.18
Koopman cGHF	DCB-SNSO	0.15	0.13	0.11	0.06	0.07
Δ SCF cGHF	DCB-SNSO	0.10	0.08	0.08	0.02	0.05
NO-QDPT HF	DCB-SNSO	-0.04	-0.03	-0.02	-0.04	0.00
NO-QDPT SCAN	DCB-SNSO	-0.01	-0.01	0.01	-0.03	0.01
NO-QDPT SCAN0	DCB-SNSO	-0.01	-0.01	0.00	-0.03	0.01

Table 2.3: Gas phase 3rd row element L_{2,3}-edge DS values for 18-electron series. All methods were computed using aug-pcX-2 basis set [361] on 3rd row elements and decontracted aug-pcseg-1 [362] for H. The experimental DS uncertainties provided for each value are 0.05 eV for Ar, 0.03 eV for HCl, 0.01 eV for H₂S, 0.05 eV for SiH₄.

full Δ cGHF. Somewhat surprisingly, the Koopman’s model reproduces the Δ cGHF DS very well, overestimating by $\lesssim 0.05$ eV. This further bolsters the claim that core-hole relaxation effects have a rather small effect on the DS for 3rd row elements. As expected, the absolute Koopman’s L₃ and L₂ CEBEs are greatly overestimated (~ 10 eV errors) due to lack of core-hole relaxation.

We next consider L-edge ionization energies and DS for 25 closed-shell, gas-phase molecules containing 3rd row elements. Violin plots of the error distributions for L_{2,3} ionization energies and the DS (compared to experiment) are reported in Fig. 2.2. In this application, the choice of optimized determinants (HF or DFT) has little impact on the DS errors. Again, unscreened X2C systematically overestimates the DS, while the screened models (DCB-SNSO and Z_{eff}) lead to much smaller errors (RMSE $\lesssim 0.06$ eV), with DCB performing slightly better than Z_{eff} . The largest DS overestimation is for Ar (highest Z). The largest underestimation is for CCl₄ (experimental DS[363] of 1.69 eV). We note that another experiment[364] reported a DS of 1.6 eV for this molecule, which is closer to the screened SOC results (as well as to the 1.6 eV separation between multiplet peaks observed in the L-edge X-ray absorption spectrum[294, 365]). This example aside, we do not observe any significant shifts in the DS (relative to the values for the simple hydrides in Table 2.3) for a specific element due to the molecular environment.

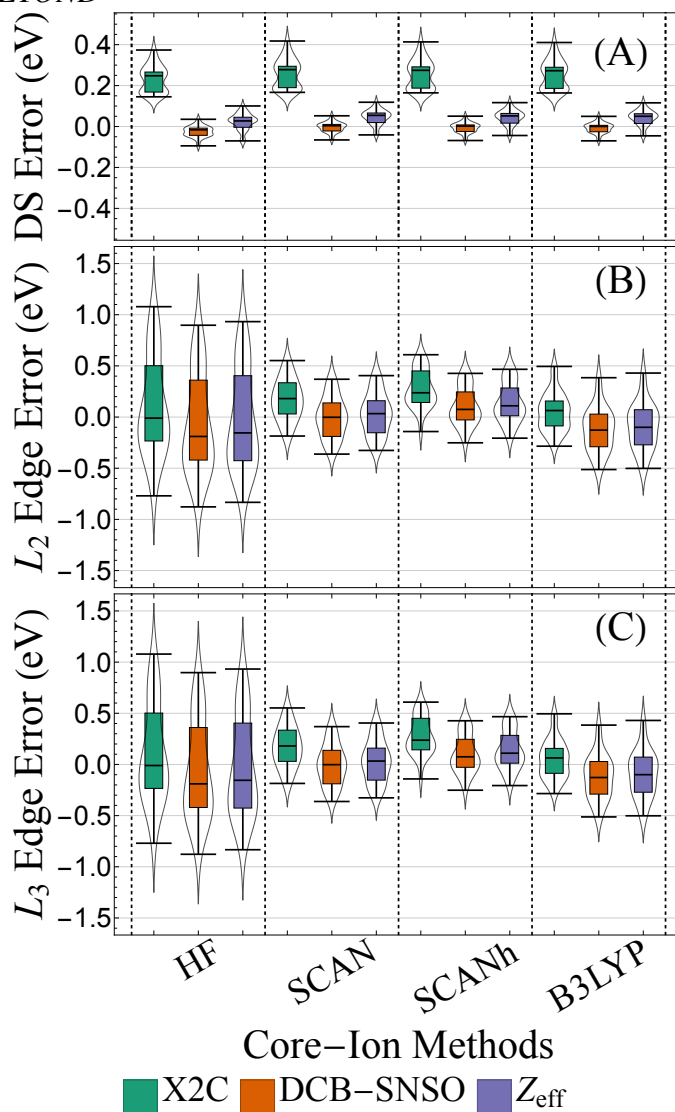


Figure 2.2: Violin plots for the gas phase 3rd row element $L_{2,3}$ -edges. Boxes span the 50% as the interquartile range with the median noted, and the underlying contours show the distribution of the data. All methods were computed using aug-pcX-2 [361] except for H which used decontracted aug-pcSeg-1 [362] basis set. Individual data points and error for 25 molecules and 8 functionals are available in the Sec. B.5 along with their experimental references. SCANh stands for SCAN with 10% exact exchange. (A) $L_{2,3}$ DS. RMSE for HF/X2C, SCAN/X2C, HF/DCB-SNSO, and SCAN/DCB-SNSO are 0.24 eV, 0.27 eV, 0.04 eV, and 0.03 eV. (B) L_2 IPs. RMSE for HF/X2C, SCAN/X2C, HF/DCB-SNSO, and SCAN/DCB-SNSO are 0.50 eV, 0.26 eV, 0.49 eV, and 0.20 eV. (C) L_3 IPs. RMSE for HF/X2C, SCAN/X2C, HF/DCB-SNSO, and SCAN/DCB-SNSO are 0.49 eV, 0.22 eV, 0.47 eV, and 0.20 eV.

In contrast to the behavior for predicting the DS, the error distributions for the $L_{2,3}$ CEBEs reveal the advantages of using DFT over HF, with most of the tested functionals (except BHHLYP) roughly halving the spread of the error distribution. Indeed, NO-QDPT/SCAN/DCB-SNSO yields an RMS error of 0.2 eV, which is comparable to results obtained for K-edges of similar molecules[177, 194] and not much larger than typical experimental uncertainties (~ 0.1 eV). B3LYP with DCB-SNSO also yields a similar performance with RMS error of 0.2 eV. These are very encouraging results. By contrast, NO-QDPT/HF/DCB-SNSO has a larger RMS error of 0.5 eV, due to lack of dynamic electron correlation. The choice of the functional matters for NO-QDPT/DFT: BHHLYP yields worse performance than the SCAN family of functionals and SCAN0 slightly degrades the good performance of SCAN. In addition, while BHHLYP mostly overestimates CEBEs, the two tested range-separated hybrids (ω B97X-D3 and ω B97X-V) tend to underestimate the CEBEs. The full results for the tested functionals not shown in Fig. 2.2 is given shown in Sec. B.5 We also stress that the success of NO-QDPT/DFT depends on more than choosing a suitable functional. It also relies on the validity of the relativistic $\hat{H}^{\text{model}}$ given by Eq. (2.14), and the quality of the NOCI subspace. For the latter, it is important to avoid linear dependencies within the NOCI subspace (some strategies for achieving this are provided in Sec. B.2).

2.3.3 L– Edges for 4th Row Main Group Elements

We next consider 2p ionization behavior for molecules containing 4th row main group elements (Table 2.4). Since gas phase experimental data is scarce, we can report results for only a few species. We restricted our testing to HF, SCAN, SCAN0 and B3LYP, based on our results for the 3rd row main group elements. The s block elements (K and Ca) behave similarly to the 3rd period elements in that unscreened X2C overestimates the DS, while DCB-SNSO is essentially quantitative. All of the tested methods yield quite accurate $L_{2,3}$ DS for K and Ca (~ 0.2 eV error). Notably, B3LYP shows slightly degraded performance in predicting L_3 ionization energies, compared to the other tested methods.

The heavier elements Zn, Ge, and Kr present a somewhat less encouraging picture, at first glance. For the DS, errors from the NO-QDPT/SCAN/DCB-SNSO model increase to as much as 1 eV for Kr. rDCB-SNSO Hamiltonian slightly degrades performance relative to DCB, while Z_{eff} is significantly poorer (Sec. B.6). While the absolute DS errors are considerably larger for these heavier elements, so too is the magnitude of the DS themselves. In percentage terms, the performance of NO-QDPT/DFT/DCB-SNSO is not significantly degraded, but the systematic underestimation hints at limitations of the hybrid protocol, the relativistic Hamiltonian, and/or the density functional. In this regard, we note that Δ cGHF calculations for the $L_{2,3}$ ionization energies of Kr find < 0.1 eV error in the DS, compared to -1.5 eV from the NO-QDPT protocol with HF/DCB-SNSO and 0.4 eV from a Koopman energy difference of neutral Kr cGHF 2p orbitals. This indicates that the interplay between SOC and orbital relaxation is potentially non-negligible for these heavier elements, and a fully variational treatment may be optimal.

The performance for $L_{2,3}$ CEBEs for molecules containing Zn, Ge, and Kr is much worse than for K and Ca. All NO-QDPT/DFT/DCB-SNSO systematically underestimates the L_3 CEBEs by as much as 6.1 eV for Kr with B3LYP. SCAN0 underestimates the least of the three, but still

		KCl	KBr	Ca	Zn	GeH ₄	GeCl ₄	Kr
Expt. L₃ (eV)		300.8 [366]	301.1 [367]	357.6 [368]	1029.1 [369]	1225.7 [370]	1228.1 [370]	1679.2 [371]
Method	Model ($\hat{H}$)	Error (eV)						
HF	X2C	-0.1	-0.3	-0.6	-0.6	-0.3	0.7	0.3
SCAN	X2C	-0.5	-0.8	-0.7	-2.8	-4.6	-4.2	-6.3
SCAN0	X2C	-0.1	-0.3	-0.4	-2.0	-3.3	-2.8	-4.4
B3LYP	X2C	-1.0	-1.2	-1.6	-4.0	-5.6	-6.9	-7.6
HF	DCB-SNSO	0.1	-0.1	-0.4	0.2	0.7	1.8	1.8
SCAN	DCB-SNSO	-0.3	-0.6	-0.5	-1.9	-3.5	-3.2	-4.7
SCAN0	DCB-SNSO	0.1	-0.1	-0.2	-1.2	-2.3	-1.7	-2.9
B3LYP	DCB-SNSO	-0.8	-1.0	-1.4	-3.1	-4.6	-5.8	-6.1

		KCl	KBr	Ca	Zn	GeH ₄	GeCl ₄	Kr
Expt. DS (eV)		2.8 [366]	2.8 [367]	3.4 [368]	23.2 [369]	31.1 [370]	30.9 [370]	52.7 [371]
Method	Model ($\hat{H}$)	Error (eV)						
HF	X2C	0.5	0.5	0.7	2.1	2.4	2.6	3.2
SCAN	X2C	0.5	0.5	0.8	2.4	2.8	3.0	3.7
SCAN0	X2C	0.5	0.5	0.8	2.3	2.7	2.9	3.6
B3LYP	X2C	0.5	0.5	0.8	2.4	2.7	2.9	3.7
HF	DCB-SNSO	0.0	0.0	0.1	-0.4	-0.7	-0.5	-1.4
SCAN	DCB-SNSO	0.0	0.0	0.2	-0.2	-0.4	-0.2	-0.9
SCAN0	DCB-SNSO	0.0	0.0	0.1	-0.2	-0.5	-0.3	-1.0
B3LYP	DCB-SNSO	0.0	0.0	0.1	-0.2	-0.4	-0.2	-0.9

Table 2.4: Gas phase 4th row element L_{2,3}-edge DS and absolute L₃ edges computed through NO-QDPT. All methods were computed using decontracted cc-pVDZ for H and Cl, decontracted aug-cc-p ω CVTZ-X2C[372] for K, Ca, and decontracted aug-cc-p ω CVTZ-DK for Zn, Ge, Br, Kr.[345, 346]

yields considerable errors. Surprisingly, HF is the best-performing method, which is presumably fortuitous, and reflects other errors already mentioned. We note that in percentage terms, the

			HF	SCAN	B3LYP	HF	SCAN	B3LYP
Expt. L_3 (eV)		OS	X2C Error (eV)			DCB-SNSO Error (eV)		
V(CO) ₄ (C ₅ H ₅)	519.6	+1	1.3	-0.6	-1.3	1.6	-0.3	-1.0
Cr(CO) ₆	582.0	0	0.3	-0.6	-1.7	0.7	-0.2	-1.3
Cr(CO) ₅ (CS)	581.7	0	0.5	-0.5	-1.6	0.9	-0.1	-1.2
Mn(CO) ₅ H	647.5	+1	0.3	-0.8	-2.0	0.8	-0.4	-1.6
Mn(CO) ₃ (C ₅ H ₅)	646.7	+1	0.5	-0.9	-2.1	1.0	-0.5	-1.7
Mn(CO) ₂ (CS)(C ₅ H ₅)	646.8	+1	0.4	-1.0	-2.2	0.8	-0.6	-1.8
Fe(CO) ₅	715.8	0	-0.3	-0.8	-2.3	0.2	-0.3	-1.8
Fe(CO) ₄ (C ₂ H ₄)	715.4	0	0.0	-1.1	-2.5	0.5	-0.6	-2.0
Fe(CO) ₄ (H) ₂	716.0	+2	1.2	-0.8	-2.2	1.7	-0.3	-1.7
Fe(C ₅ H ₅) ₂	713.1	+2	2.5	-0.9	-2.1	3.0	-0.4	-1.6
Fe(H ₃ CC ₅ H ₅) ₂	713.0	+2	2.3	-1.1	-2.3	2.8	-0.6	-1.8
Co(CO) ₃ (NO)	786.9	-1	0.3	-1.0	-2.6	0.8	-0.4	-2.0
Co(CO) ₄ (H)	786.9	+1	0.1	-0.8	1.5	0.7	-0.2	1.5
Co(CO) ₂ (C ₅ H ₅)	786.3	+1	-0.3	-1.6	-3.1	0.3	-1.0	-2.5
Ni(CO) ₄	861.2	0	-2.5	-1.4	-3.3	-1.9	-0.7	-2.6
Ni(PF ₃) ₄	862.0	0	-2.1	-2.0	-3.6	-1.5	-1.3	-3.0
Ni(acac) ₂	860.5	+2	3.3	-2.3	-3.2	4.0	-1.6	-2.5

Table 2.5: Transition Metal (TM) L_3 ionization energies for complexes that satisfy the 18-electron rule, calculated through NO-QDPT. The transition metal oxidation states (TM OS) are also provided. All methods were computed using decontracted aug-cc-p ω CVTZ[373] on TM centers and decontracted aug-cc-pVDZ basis set on others. The acetylacetonate ligand is abbreviated as acac.

worst NO-QDPT/DFT/DCB-SNSO error is less than 0.4% for Kr (B3LYP). More importantly, the NO-QDPT/DFT/DCB-SNSO error in the *shift* between GeH₄ and GeCl₄ L_3 CEBEs is only 0.2 eV out of 2.4 eV, so the theory still appears promising for chemical shift effects, despite the noticeable degradation in performance in predicting absolute CEBEs for these heavier elements.

2.3.4 L– Edges for 1st Row Transition Metals

The differing quality of results for K/Ca versus Zn/Ge/Kr makes assessment of the performance of NO-QDPT/DFT for the first row transition metals very interesting. We first examine L_3 CEBEs where there is more available experimental data, followed by DS results on a few species with

experimental values. Tables 2.5 and 2.6 present the L_3 ionization energies in 18-electron and non-18-electron transition metal complexes, respectively.

We first discuss the case of the 18-electron complexes (which presumably have less challenging ground state electronic structure). From Table 2.5, we see performance that roughly mirrors what was reported for the 4th row main group elements above. Notably NO-QDPT/SCAN/DCB-SNSO outperforms the corresponding HF approach, though both underestimate the CEBEs. As already seen above, the underestimation grows towards $> 1\text{eV}$ for TMs with increasing atomic numbers, such as Co and Ni, with percentage errors also increasing (albeit more slowly). Notably the accuracy of B3LYP is worse than SCAN both with or without screening of SOC. The situation is better for the relative chemical shifts than absolute CEBEs, with errors roughly halved. It is interesting to note that the errors in relative chemical shifts for a given element are little changed by replacing SCAN by HF, indicating that effects other than the quality of orbitals are responsible for these errors.

				HF	SCAN	B3LYP	HF	SCAN	B3LYP
L_3 Expt. (eV)		e^- Count	OS	X2C Error (eV)			DCB-SNSO Error (eV)		
TiCl ₄	465.4 [374]	8	+4	6.1	-0.9	-1.0	6.4	-0.6	-0.7
Ti(NO ₃) ₄	466.8 [375]	8	+4	6.7	-1.9	-1.5	7.0	-1.6	-1.2
VOF ₃	527.1 [376]	10	+5	6.8	-1.3	-1.2	7.1	-0.9	-0.9
VF ₅	528.9 [376]	10	+4	7.9	-1.4	-1.1	8.3	-1.0	-0.8
Ni(C ₅ H ₅) ₂	859.9 [377]	20	+2	0.8	-2.2	-3.6	1.5	-1.6	-2.9

Table 2.6: Transition Metal (TM) L_3 ionization energies for non 18-electron complexes computed with NO-QDPT. The electron-count of the given TM complexes as well as the oxidation state (OS) of the TM centers are given. All methods were computed using decontracted aug-cc-pwCVTZ[373] on TM centers and decontracted aug-cc-pVDZ basis set on others.

We only have data for five non-18-electron complexes (Table 2.6) so it is hard to draw general conclusions. However in the 4 electron deficient (formally d^0) complexes, use of HF orbitals causes very large 7-8 eV overestimates, which are greatly reduced by use of DFT. There is also very little data with which to assess the performance of NO-QDPT/DFT for 2p ionization DS (Table 2.7; two Fe DS were taken from the lowest dipole-allowed transitions of the gas phase L-edge Fe(CO)₅ and Fe(C₅H₅)₂ XAS spectra). The DS results appear similar to those discussed previously for 4th row main group elements. The best accuracy is achieved via NO-QDPT/SCAN/DCB-SNSO, with slight error increases across the 1st TM series, as was also seen for L_3 edge prediction.

		HF	SCAN	B3LYP	HF	SCAN	B3LYP
Expt. L-edge DS (eV)		X2C Error (eV)			DCB-SNSO Error (eV)		
Ti(NO ₃) ₄	5.9 [375]	0.4	0.5	0.5	-0.4	-0.4	-0.4
Cr(CO) ₆	8.8 [378]	0.6	0.7	0.6	-0.6	-0.5	-0.5
Fe(CO) ₅	12.3 [379]*	1.0	1.2	1.1	-0.5	-0.4	-0.4
Fe(C ₅ H ₅) ₂	12.4 [379]*	1.0	1.1	1.1	-0.5	-0.4	-0.4
Ni(acac) ₂	17.4 [380]	1.3	1.5	1.4	-0.7	-0.5	-0.6

Table 2.7: Transition Metal (TM) DS results computed with NO-QDPT. All methods were computed using decontracted aug-cc-p ω CVTZ[373] on TM centers and decontracted aug-cc-pVDZ basis set on others. The acetylacetonate ligand is abbreviated as acac. * Fe L-edge DS values are taken from the 1st dipole allowed *excitations* of Ref. [379], as results from CEBEs were not available.

2.3.5 M- and N- edges of 4th Row and Beyond

We next explore the performance of NO-QDPT/DFT in predicting CEBEs of d-electrons where SOC couples 5 different spatial orbitals, leading to $d_{5/2}$ and $d_{3/2}$ sublevels. Table 2.8 tabulates M/N-edge SOC splittings and the smaller CEBE of the multiplet (*i.e.*, M_5 of $M_{4,5}$, N_5 of $N_{4,5}$). The DS results again show improved performance of DCB-SNSO in NO-QDPT over X2C, as well as insensitivity to choice of functional for orbital optimization. The CEBEs, however, are systematically underestimated in virtually all cases, similar to behavior observed for the first row TM ligand complexes (Table 2.5). DFT mostly improves over HF but is worse for Kr M_3 , Cd M_5 and CH₃I M_5 . This again demonstrates that alternative approaches towards modeling SOC is needed for these heavier elements. rDCB-SNSO yields very similar results to universal DCB-SNSO for the splittings and the absolute edges. Finally, we note that the NO-QDPT/DFT results for the Kr M_3 edge are particularly poor.

2.3.6 Molecular field splitting in CH₃I, HBr and HCl

The lack of spherical symmetry in molecular environments formally breaks the degeneracy within a given SOC split multiplet like the $2p_{3/2}$ orbitals. The resulting molecular field splitting is often smaller than or comparable to the lifetime width of the XPS spectral feature, and as a result is difficult to experimentally to observe. Throughout this work, we have therefore averaged over all possible eigenvalues within a multiplet (such as all four Cl $2p_{3/2}$ hole states in HCl) to compute DS splittings or CEBEs. For a few small molecules like HBr[327] and HCl[384] however, it is possible to fit individual ionization contributions to an observed multiplet feature (with tolerable error bars ≤ 0.1 eV). As previously noted, a limitation of NO-QDPT is that it cannot account for dynamic electron correlation contributions to the molecular field induced splitting. These

		Kr	HBr	CH ₃ Br	Kr	Cd	CH ₃ I	CH ₃ I	Xe
		M ₃	M ₅	M ₅	M ₅	M ₅	M ₅	N ₅	N ₅
Expt. M/N IP (eV)		214.4	77.3	76.2	93.8	412.9	626.8	56.6	67.5
		[381]	[327]	[327]	[356]	[369]	[382]	[383]	[356]
Method	Model ($\hat{H}$)	Error (eV)							
HF	X2C	2.5	-2.0	-2.1	-1.9	-1.3	-1.0	-1.4	-1.3
SCAN	X2C	-6.2	-1.1	-1.1	-1.1	-2.7	-3.9	-0.6	-0.6
SCAN0	X2C	-3.8	-1.0	-1.0	-1.0	-2.0	-2.8	-0.5	-0.5
B3LYP	X2C	-6.7	-0.8	-0.8	-0.9	-3.1	-4.6	-0.7	-0.8
HF	DCB-SNSO	2.8	-1.8	-1.9	-1.7	-0.4	0.3	-1.2	-1.1
SCAN	DCB-SNSO	-6.0	-0.9	-0.9	-0.9	-1.8	-2.6	-0.5	-0.4
SCAN0	DCB-SNSO	-3.6	-0.8	-0.8	-0.8	-1.2	-1.5	-0.3	-0.3
B3LYP	DCB-SNSO	-6.5	-0.6	-0.6	-0.7	-2.2	-3.3	-0.6	-0.6

		Kr	HBr	CH ₃ Br	Kr	Cd	CH ₃ I	CH ₃ I	Xe
		M _{2,3}	M _{4,5}	M _{4,5}	M _{4,5}	M _{4,5}	M _{4,5}	N _{4,5}	N _{4,5}
Expt. SOC Split (eV)		7.8	1.0	1.0	1.3	6.8	11.5	1.7	2.0
		[381]	[327]	[327]	[356]	[369]	[382]	[383]	[356]
Method	Model ($\hat{H}$)	Error (eV)							
HF	X2C	0.5	0.5	0.5	0.6	2.8	3.0	0.4	0.4
SCAN	X2C	0.6	0.5	0.5	0.6	2.9	3.1	0.5	0.5
SCAN0	X2C	0.5	0.5	0.5	0.6	2.9	3.0	0.4	0.5
B3LYP	X2C	0.6	0.5	0.5	0.6	2.9	3.1	0.5	0.5
HF	DCB-SNSO	-0.2	0.0	0.0	0.0	0.7	-0.3	-0.1	-0.1
SCAN	DCB-SNSO	-0.1	0.0	0.0	0.0	0.7	-0.2	0.0	0.0
SCAN0	DCB-SNSO	-0.1	0.0	0.0	0.0	0.7	-0.2	0.0	-0.1
B3LYP	DCB-SNSO	-0.1	0.0	0.0	0.0	0.7	-0.2	0.0	0.0

Table 2.8: SOC splittings of M/N edges and corresponding absolute IP for selected gas phase molecules containing beyond 4th row elements, computed through NO-QDPT.

molecules therefore present an opportunity to test the practical implications of neglecting this effect on the quality of predicted XPS spectra.

CH ₃ I N _{4,5} [383]				HBr M _{4,5} [327]				HCl L _{2,3} [384]			
State	Expt.	HF	SCAN	State	Expt.	HF	SCAN	State	Expt.	HF	SCAN
E _{1/2}	0.00	0.00	0.00	Δ _{5/2}	0.00	0.00	0.00	Π _{3/2}	0.00	0.00	0.00
E _{3/2}	0.19	0.18	0.17	Π _{3/2}	0.18	0.18	0.18	Σ _{1/2}	0.09	0.03	0.04
E _{1/2}	0.35	0.29	0.29	Σ _{1/2}	0.30	0.31	0.30	Π _{1/2}	1.66	1.61	1.64
E _{3/2}	1.73	1.69	1.73	Δ _{3/2}	1.08	1.06	1.07				
E _{1/2}	1.93	1.91	1.95	Π _{1/2}	1.30	1.29	1.29				
Γ	~ 0.2			Γ	~ 0.2			Γ	~ 0.1		

Table 2.9: Energies (in eV, relative to the lowest energy feature) of the different core-hole states arising from molecular field induced loss of spherical symmetry for the N_{4,5} edge of CH₃I, M_{4,5} edge of HBr and L_{2,3} edge of HCl. The experimental core-hole state lifetime widths Γ are also reported. All calculations utilize NO-QDPT with the DCB-SNSO model.

The relative energies of the molecular field induced N_{4,5} edge of CH₃I, M_{4,5} edge of HBr and L_{2,3} edge of HCl are reported in Table 2.9. The agreement is excellent for CH₃I and HBr, with similarly good performance obtained from CH₃Br. However the molecular field splitting is significantly underestimated for HCl, indicating dynamic correlation effects matter more for this system. This means little in practical terms on account of the ~ 0.1 eV lifetime broadening of the associated spectral features, which makes them difficult to resolve within the L₃ peak, but nonetheless indicates a potential need for caution in modeling very small molecular field induced splittings. This behavior may be analogous to stronger correlation effects in transition metal complexes with smaller ligand field splittings[334, 385]. On the other hand, it is encouraging that the larger molecular field splittings in the XUV range (Br M_{4,5} edge and I N_{4,5} edge) are reproduced well by NO-QDPT, as these are more likely to be experimentally resolvable.

2.4 Conclusions

In this work, we have proposed, implemented, and benchmarked a new protocol to extend orbital optimized DFT (OO-DFT) to enable quite accurate yet tractable calculations of molecular core-electron binding energies (CEBEs) and doublet splittings (DS) associated with non-zero orbital angular momentum, when important spin-orbit coupling (SOC) effects are at play. This non-orthogonal quasi-degenerate perturbation theory (NO-QDPT) uses OO-DFT to optimize the orbitals of all determinants needed to span the space of possible holes (e.g. 3 sets of spatial orbitals span the 6-dimensional Hilbert space of a 2p hole). Those determinants are used in non-orthogonal configuration interaction (NOCI) to determine the split sublevels, using a relativistic 1eX2C Hamiltonian which includes the SOC effects with screening. The diagonal matrix elements are shifted

using the average of the OO-DFT calculations.

Our main results and conclusions are as follows:

1. The SNSO family of SOC Hamiltonians in combination with NO-QDPT/SCAN yielded highly accurate $L_{2,3}$ ionization energies and DS for 3rd row main group elements. Absolute CEBEs show < 0.2 eV error, while the DS values have even smaller (~ 0.04 eV) errors.
2. NO-QDPT/SCAN demonstrates semi-quantitative accuracy on $L_{2,3}$ CEBEs and DS of 4th row s-block elements, with errors gradually increasing with atomic number. Results for 3d transition metal complexes show a similar trend.
3. There are several potential sources of error in the NO-QDPT/DFT approach, including density functional errors, the quality of the core-hole state subspace, errors arising from the combination of NOCI and DFT, and the treatment of the scalar and vector relativistic Hamiltonian terms. Further work is needed to unravel their relative contributions to the largest errors seen for $L_{2,3}$ CEBEs and DS of transition metal atoms and heavier elements.

Our promising 2p core ionization results for the lighter elements motivate future work on extending NO-QDPT to L-edge excitations. We intend to approach this challenge by extending 1-center NOCIS[183]. We are also interested in improved approaches for generating the core-hole orbitals. An important question is better understanding the origin of the poorer performance of NO-QDPT/DFT for L-edge CEBEs. Would a better relativistic Hamiltonian improve these results or are other missing effects at play?

Supporting Information

Original versions of both main text and the Supporting Information can be accessed in the online published version of Ref. [386], which contains full data table containing computed values as well as geometry files used in this work.

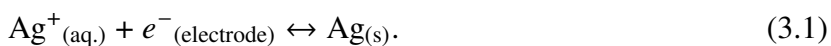
Chapter 3

Understanding Ion-transfer Reactions in Silver Electrodeposition and Electrodeposition

3.1 Introduction

Electrochemical reactions necessarily involve the transfer of both electrons and ions. While there has been tremendous progress developing quantum-mechanical theories of electron transfer, [387, 388] understanding the concomitant ionic reactions is challenged by the molecular complexity of electrified interfaces. A fundamentally important class of reactions are faradaic processes, which involve generation or consumption of ions at solid/solution interfaces. The study of such ion-transfer reaction is difficult due to the atomic/molecular complexity of the solid-liquid interface that is the electric double layer. [209] There is no analytical theory that captures the complex behavior at the interface to predict reactivity and rates. [207] Yet advances in many important applications, such as chemical energy conversion to fuels [5, 389–392], durable rechargeable batteries [393–395] as well as corrosion control (estimated to cost 3 – 4% of global GDP), [396] could greatly benefit from fundamental understanding of these interfacial reactions and their microscopic mechanisms, which will provide insights on how to control their rates, selectivity, stability, and/or activity.

Fundamentally, even the molecular details of the simplest reactions, *i.e.*, anodic dissolution and deposition involving solvated monovalent cations such as Ag^+ have been described as an “enigma” [397]. The factors that control the reaction barriers for the simplest cases, let alone for divalent species like Zn^{2+} and other technologically relevant rare-earth cations, [398] are surprisingly less studied. To fill this gap, our work will focus on a suitable model system, specifically the chemically reversible dissolution/deposition of Ag:



Eq. (3.1) is thought to be very fast, [399] although the precise rate constant remains unknown. The mechanism for silver corrosion was proposed by Gerischer in the 1950s, suggesting that the slow

initiation step is migration of an atom to a terrace site, to be followed by facile dissolution. [400] The fast rate itself however is not intuitive [397, 399] because the hydration energy of Ag^+ is ~ 5 eV and since water adsorbs weakly to the metal surface, a large free energy barrier might be expected due to desolvation at the interface. Local electric fields (important in catalysis generally [401–403]) and thus anodic (for dissolution) and cathodic (for deposition) applied potentials are surely critical stabilizing factors, but a molecular picture of the nature of the departing/approaching metal species (*i.e.*, charge and solvation state) remains poorly understood. To address these gaps, our work presents computational results that accurately capture the electronic structure free energy changes as a function of ion-surface separation and applied bias.

The multiscale complexity of the solid-liquid interface in both length and time scales prevents first principles simulations of deposition and dissolution in full dimensionality. One tractable approach is to employ classical molecular dynamics (MD) calculations or Monte Carlo (MC) sampling schemes, informed by quantum chemistry calculations as well as experimental data. [399, 404–407] These studies yielded insights into ion-transfer reactions such as underpotential deposition (UPD) of hydrogen on Pt(111) [404], concentration and anion co-adsorption effects of Cu UPD on Au(100) [406], corrosion mechanism [399], and comparison of corrosion inhibitors [405, 407]. Quantum modeling of corrosion via density functional theory (DFT) has generated quite accurate Pourbaix diagrams and calculations of bulk properties. [408–414] Other quantum-based corrosion modeling focused on solvent and applied electric field effects on potential curves for surface atom removal, using constrained optimizations. [415, 416] A proposed solution to the enigma of fast Ag^+ dissolution emerged from DFT calculations that identified a long-range, favorable interaction between the atomic 5s orbital and the metal sp band. [399] Whilst considerable insight has been gained, there is a significant gap in that these studies omit the role of electrolyte and applied electrode potential which are both central to electrochemical dissolution and deposition.

In this work, we report a computational study of electrochemical Ag anodic dissolution/deposition using, for the first time in the context of ion-transfer reactions, the constant electrode potential (CEP) model for simulations and transient voltage-step measurements. The CEP protocol [235, 417] is a form of grand-canonical DFT (GC-DFT) [242] that iteratively aligns the Fermi level of the metal with the applied electrode potential to allow electronic structure of the electrode and interface to respond to applied bias. This model is paired with the linearized Poisson-Boltzmann (LPB) implicit solvation model [418, 419] that provides counterions, in addition to the explicit first-solvent-shell waters to account for molecular desolvation/resolvation. The simulations yield free energy profiles for dissolution/deposition of an Ag^+ ion, and physical insights into the nature of bias and field-driven effects on the barrier. Information on distance-dependent electron transfer, ion desolvation/resolvation and facet dependence is also obtained. These new data and insights into the bias-dependent barrier to the ion-transfer reaction in Ag deposition/dissolution helps to build a knowledge base that is relevant to corrosion science, as well as the development of more durable electrocatalysts and light absorbers in solar fuel systems.

3.2 Computational Details

Solvation Model Design. The Q-Chem [335] package was used to determine the appropriate number of explicit waters. The Polarizable Continuum Model (PCM) [420, 421] (dielectric constant 78.39) was utilized. Starting from the WATER27 [422, 423] structures, an Ag cation was coordinated to varying numbers of water molecules. ω B97M-V [119]/def2-SVPD [341, 424] was used for structure optimization, followed by a single-point calculation with def2-TZVPPD [341, 424] for energy calculation. Effective core potentials [425] were used for Ag. As shown in Table C.1, two explicit water molecules is the minimum number needed to adequately reproduce the hydration energy of Ag^+ in the implicit solvent/electrolyte model. This was then employed for all subsequent corrosion/deposition simulations.

Supercell Design. Supercell calculations used Vienna *Ab Initio* Simulation Package (VASP) [426–429] with the revised Perdew–Burke–Ernzerhof (RPBE) density functional [88] and the projector augmented wave (PAW) pseudopotentials. [430] No dispersion corrections were employed, to avoid unphysical overbinding of the corroding atom in implicit solvent/electrolyte (Sec. C.4). The lattice constant 4.208 Å for Ag fcc cell was determined through ionic relaxation with variable volume size with a $12 \times 12 \times 12$ Monkhorst-Pack (MP) grid. [431] The electronic energy and atomic force convergence were 10^{-6} eV and 10^{-4} eV/Å, respectively. A plane-wave cut-off of 600 eV and a Gaussian smearing width of 0.05 eV were used. For the ideal surface (Ag_{24}), the Ag (100) supercell contained 3 layers of 8 Ag atoms with a total of 24 atoms, and a continuum solvent/electrolyte of ~ 20 Å was placed between two images in the surface normal direction to give a total cell height of 30 Å. This cell size was confirmed through its accurate prediction of the potential of zero charge (PZC). (Experimental PZC of Ag(100): -0.609 V vs. SHE [218], Computed PZC: -0.603 V vs. SHE).

The single adatom model (Ag_{25}) was constructed starting from this structure. Implicit solvent and electrolyte were modeled via VASPsol [418, 419, 432] package. Relative permittivity $\epsilon_b = 78.4$ and the Debye Length $\kappa_b^{-1} = 3.000$ Å were used, equivalent to 1.0 M monovalent 1-to-1 electrolyte. The cavitation energy was neglected by setting the surface tension parameter τ to 0.000 due to numerical instabilities. The Grand Canonical Free Energy obtained included the finite cell-height correction. [433]

CEP Calculations. The CEP calculations were carried out with VASP/VASPsol and Atomic Simulation Environment. [434] The theoretical absolute potential of the SHE ϕ_{SHE} was 4.43 eV. [435, 436] The convergence criteria for the electrode potential, electronic energy, and the atomic force was 10^{-4} V (10^{-3} V for challenging cases), 10^{-6} eV, and 0.003 eV/Å (0.005 eV/Å for challenging cases), respectively. For the challenging convergence cases, loosened criteria were used and verified against the nearby data points. An MP grid of $6 \times 6 \times 1$ was used. Plane-wave cut-off energy, Gaussian smearing width, and the VASPsol parameters were all identical to that used in the supercell design.

Transition State Search. The initial structure was first optimized at $z = 6\text{\AA}$ from the surface with the optimized two-water solvation shell. Subsequent calculations reduced z repeatedly, always starting from the previous converged result, apart from translating $\text{Ag}(\text{H}_2\text{O})_2$ by the step, δz to yield the sequence of constrained optimizations. The procedure was reversed when hysteresis was observed, to get the lower energy structure. Constrained optimizations (Selective Dynamics in VASP) were utilized — the approaching/departing Ag atom was only allowed to relax in surface parallel direction. All coordinates of the water solvation shell were left free. Due to convergence difficulties, we chose to fix the coordinates of all other bulk Ag atoms at the values from the parent model.

Atomic Partial Charges. The partial charges were calculated with iterative Hirshfeld (HI) partitioning [437, 438] with the damping function parameter of 1.000. The CEP-optimized structures were used with the final number of electrons.

3.3 Results and Discussion

While we will use the terms corrosion and electrodisolution interchangeably, we emphasize that our work concerns dissolution of Ag(s) under applied electrochemical bias, rather than its kinetically slower degradation under typical open-circuit conditions.

3.3.1 Bias-dependent simulations of adatom dissolution/deposition

The most reactive surface atoms are undercoordinated, such as at kinks and steps. A single top-layer atom plays that role in a model closed-packed Ag(100) surface. In brief, the simulation protocol involves constrained geometry optimizations on a periodic unit cell of 25 Ag atoms (24 bulk in 3 layers of 8 atoms, 1 adatom) and 2 H_2O molecules, where the z coordinate of the adatom (corresponding to the surface normal direction) is fixed. The electrons are self-consistently coupled to a reservoir at the applied potential, leading to loss of electrons at positive bias and partial charges. Although the coordination number of the Ag^+ ion has been both experimentally [439, 440] and computationally [441, 442] characterized as four, we find that only two explicit H_2O molecules are necessary to describe Ag^+ solvation *on top of* the linearized Poisson-Boltzmann model, as detailed in Sec. C.1.2. Full details of the periodic DFT approach, the treatment of applied bias, continuum solvent and electrolyte, and the optimizations are given in the Computational Details section. The simulations yield bias-dependent free energy profiles for the corrosion/deposition of the constrained adatom, as shown in Figure 3.1a. Three illustrations of the resulting optimized structures are shown on the right-hand side (Figures 3.1d to 3.1f). The top-center panel shows the bias-dependence and distance-dependence of the oxidation state of the departing Ag atom, while the lower-center panel shows how the bulk charge depends on the same variables (Figures 3.1b,c).

Focusing on the ΔG curve (Fig. 3.1a), we first note that this simulation yields bias-dependent thermodynamics and kinetics that are qualitatively consistent with experimental information. Regarding thermodynamics, given that the standard reduction potential of Ag is 0.80 V vs. SHE, [443]

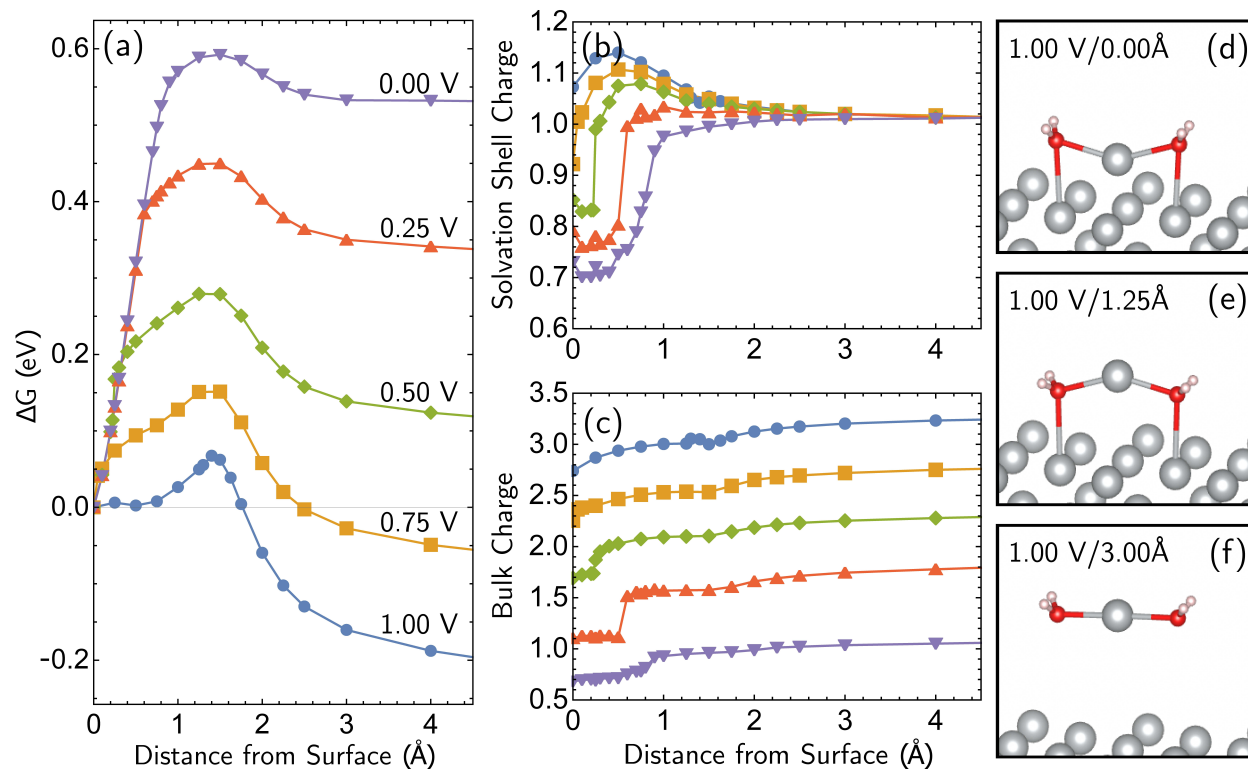


Figure 3.1: Simulations of adatom (single top-layer Ag atom) corroding from Ag(100) as a function of anode applied bias. (a) Computed change in free energy, ΔG with respect to distance from surface of the adatom (all other coordinates optimized for each constrained value of the z position of the adatom (relative to its equilibrium bound position)). Data extends to 6 Å but is not shown. (b-c) The partial charge on the adatom and its two first solvent shell water molecules, and the net charge of the remaining surface atoms. The sum of two partial charges is equal to the total charge of the cell for each data point. (d-f) Examples of optimized structures showing the development of the characteristic linear solvent structure associated with the free ion as a function of adatom displacement from the surface.

the favorability of the dissociated Ag^+ ion described by the free energy curves at positive 1.00 V and 0.75 V is very reasonable. The activation barrier of the corrosion is also qualitatively correct. The activation barrier at 1.00 V vs. SHE is 0.068 eV (6.8 kJ/mol), which corresponds to a 298 K turnover frequency (via transition state theory) of $4 \times 10^{11} \text{ sec}^{-1}$. This indicates that the reaction is very fast, which is consistent with the experimental observations. The calculated barrier height for 1.00 V vs. SHE is also in qualitative agreement with previous Potential of Mean Force (PMF) results of Pinto and co-workers. [399] We note that the PMF calculation considers the role of electrodes indirectly whereas our CEP calculations consider them explicitly in the free energy. We also note that the turnover frequencies reported may be affected by the entropic contributions from the solvation shell and surface.

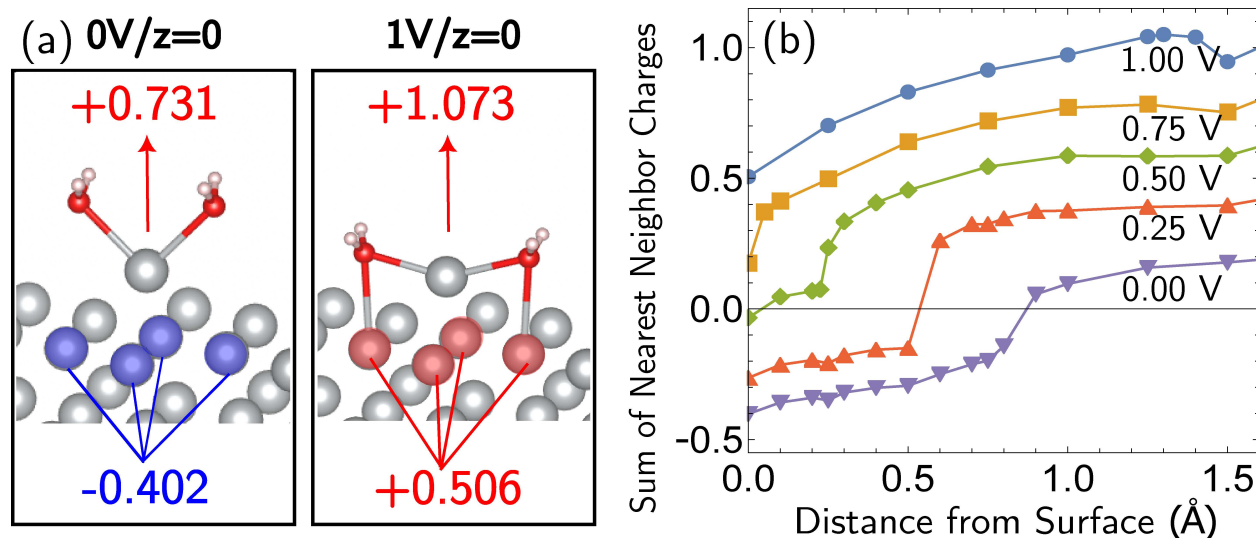


Figure 3.2: “Image”-type charge interaction in the four surface atoms that are the nearest neighbors of the adatom (same system as Figure 3.1). (a) Schematic of the partial charge formation at 0.00 V and 1.00 V optimized (undisplaced) structures of surface plus adatom and two explicit waters, respectively. The top number is the sum of the charges on the adatom and its two waters whereas the bottom number is the sum of the charges on the four nearest neighbor surface Ag atoms. A negative “image”-type charge is formed under the 0.00 V conditions, in contrast to 1.00 V. (b) The dependence of the local surface charge of the four neighbor Ag atoms on the constrained vertical displacement of the adatom, for five different applied biases. These curves show that negative “image”-like character is present at $z = 0$ for 0.00 and 0.25 V. More positive voltages suppress this local negative charge and cause increasingly positive local surface charge.

Given the unimolecular nature of the reaction, we utilized the Butler-Volmer model [224] to extract further key characteristics via

$$\Delta G_f^\ddagger = \Delta G_{\text{eqb}}^\ddagger - e\eta\alpha_c \quad (3.2)$$

where $\Delta G_{\text{eqb}}^\ddagger$ is the equilibrium activation barrier, α_c the transfer coefficient, and $\eta = \Phi - \Phi_{\text{eqb}}$ is the overpotential relative to the equilibrium electrode potential, Φ_{eqb} . Eq. (3.2) is, in principle, analogous to the phenomenological Butler-Volmer equation for the exchange current density which will be used later in this work. It is worthwhile to mention the related Brønsted-Evans-Polyani (BEP) model which also posits a linear connection between activation barrier and energy change, and has been extensively used in surface chemistry. [444] Using a linear fit of the five reaction energies and five activation barriers from each simulated electrode potential, the resulting value of 0.68 V vs. SHE for Φ_{eqb} was obtained ($R^2 = 0.994$), which is in reasonable agreement with the experimental value of 0.80 V vs. SHE measured for Ag(100) facet in aqueous solution. [218] Indeed a simulated value less than experiment may be sensible given that the simulation is dissolving the last, most ready-to-detach atom on an otherwise perfect surface. The other parameters of Eq. (3.2)

Voltage vs. SHE	Voltage vs. $\Phi_{\text{bulk, eqb}}$
1.00 V	0.18 V
0.75 V	-0.07 V
0.50 V	-0.32 V
0.25 V	-0.57 V
0.00 V	-0.82 V
Calculated bulk Ag Redox Potential $\Phi_{\text{bulk, eqb}}$: 0.82 vs. SHE	
Theoretical work function of the SHE: -4.43 eV	

Table 3.1: Potentials explored for Ag ion-transfer modeling.

that were determined from the fit are $\Delta G_{\text{eqb}}^{\ddagger} = 0.21$ eV ($R^2 = 0.987$) and $\alpha_c = 0.54$ ($R^2 = 0.995$). In order to provide a reference point for the Φ_{eqb} within the computational approach used, we also calculated the bulk reduction potential of Ag(s)/Ag⁺ via a thermochemical cycle with conventional DFT and obtained 0.82 V vs. SHE, in close agreement to the experimental value. (Sec. C.2.1) The difference of the potentials explored in this work, with respect to this bulk reduction potential, is reported in Table 3.1.

What is the molecular origin of the bias-dependent thermodynamics and kinetics discussed above? Within our simulations, the answers for thermodynamics and kinetics are largely the same, because (as seen in Figure 3.1a) the change in the forward barrier for anodic dissolution tracks the change in free energy between reactants and products. The strong bias-dependence of the energy change for displacements between 0 and 1.5 Å has several synergistic contributions. Since the 0 → 1.5 Å displacement is breaking the metal-metal bond to the Ag adatom, the first key factor is the weakening of Ag-surface bond by positive applied voltages. The center panels of Figure 3.1 (Figures 3.1b,c) reveal that the Ag adatom and its two associated H₂O molecules carry a positive charge at all voltages, but for $z = 0$ that charge is between 0.3 and 0.4 e more positive at 0.75 V and 1.00 V versus open circuit. Furthermore, that net charge in fact is slightly larger than +1 at the two most positive voltages. In other words, the adatom complex is pre-oxidized *before* displacement away from the surface at 0.75 V and 1.00 V, partly due to polarization and electron-transfer between Ag(100) and the interfacial waters that solvate the incipient Ag⁺ ion that thus take on H₂O^{δ+} character. By contrast, at the lower voltages, the lower net charge of the Ag adatom is associated with stronger binding to the surface by the Ag adatom. With lower bias, the thermodynamic price of increasing that net charge can no longer be offset by stabilization from partial solvation at the interface.

Beyond loss of binding due to surface charging, there is a second factor strengthening the adatom-bulk interaction for open circuit and low positive biases. As shown in Figure 3.2, the simulations predict the formation of a net negative charge on the four surface atoms closest to the

Ag adatom for 0.00 and 0.25 V biases, contrary to the clear partial positive charge on the adatom complex even at zero bias, as established on the top central panel of Figure 3.1. The opposing signs of the local charges resemble those of the image charges introduced in introductory electrostatics – in order to calculate the field generated by a point charge above an infinite conductor, a point charge with an opposite sign and an equal magnitude is assumed to be induced inside the conductor. The “image”-like charge in our Ag model is similar to this simple example sans the equal magnitude, and this induces an electrostatic attraction between the adatom and the nearest neighbors which must be overcome in order to remove the adatom under zero or low positive bias. The presence of this locally electron-rich Ag atoms is particularly special given that the total charge placed on the cell is positive. This highlights the importance of capturing the quantum mechanical interaction which can influence the microscopic dipole. By contrast, the local surface charge becomes positive at more positive biases, and its electrostatic interaction with the adatom complex becomes repulsive.

The bias-dependence matches our intuition since the more positively charged the surface, the more energetically costly it will be to create a local negative charge. Conversely local positive surface charge at corroding potentials is partially stabilized by solvent and electrolyte effects. As also shown in Figure 3.2a, molecular water more closely approaches the electrode surface at 1.00 V than 0.00 V, and provides favorable charge-dipole interactions. Similar considerations apply to electrolyte anions (implicitly treated in our simulations).

Additional points can be made on the effects of the molecular solvent along the reaction coordinate for dissolution/deposition. Two solvent molecules plus continuum solvation yield reasonable hydration energies for Ag^+ (Sec. C.1.2) and those molecules coordinate the ion optimally in a linear geometry as shown in the bottom right panel of Figure 3.1 (Fig. 3.1f). By contrast, the surface coordination at $z = 1.25 \text{ \AA}$ involves waters closer to the surface than Ag^+ , which then reverses as the adatom binds to the surface to yield a v-shaped coordination geometry. Comparison against a fully implicit model (Sec. C.1.1) shows that the explicit solvent molecules do not greatly affect the reverse barrier (for deposition), showing that their main role is stabilizing the initial dissociation of the ion. The origin of our calculated corrosion barrier is therefore electronic rearrangements, including the breaking of the adatom-surface bond, and the image charge interaction at low biases. We note that the free energy change ΔG reported in this work is the electrostatic free energy change that includes the contribution from the implicit solvent/electrolyte but not the Gibbs Free energy change. In fact, entropic effects associated with the solvent rearrangement (except for the important electrostatic contribution) are not captured in our simulations. It has been previously observed that rigid rotor / harmonic oscillator approximations to add entropic contribution may lead to overestimation of free energy in solvated environments, due to reduced rotational and translational degrees of freedom. [445, 446] In addition, we are mostly interested in the change in the free energy between the initial and final states in this work, which will render the entropic contribution be even smaller. Thus we view it as reasonable (as well as necessary for practical reasons) to neglect the entropic contribution for our simulations.

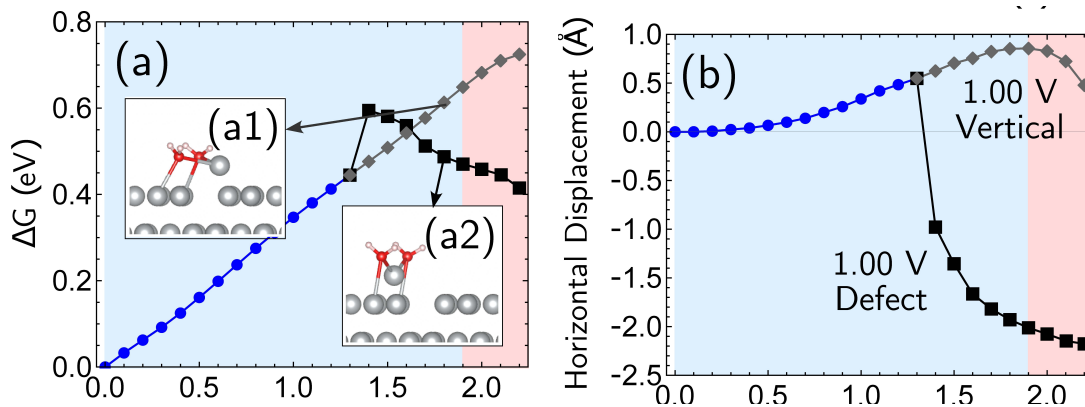


Figure 3.3: Simulation results for the removal of the first atom from a perfect Ag(100) surface, at 1.00 V vs. SHE. The horizontal drift of the departing atom is confined to one dimension, and the drift is plotted as a signed quantity. The data reveals two pathways, a more favorable pathway that creates a surface defect (adatom) and a less favorable pathway corresponding to direct removal. (a) Two representative structures optimized at 1.7 Å vertical distance from the original position are shown as insets in the top plot of free energy change versus displacement of the atom from the surface. Apart from this one constraint, all other geometric parameters were fully optimized. (b) The bottom plot shows the horizontal (in surface plane) displacement for the two paths.

3.3.2 Simulating defect-formation in corrosion

Having established the qualitative accuracy of the simulation protocol against experiment, we next report simulations on different surface morphologies to explore whether there are any interesting changes in the predicted pathways for ion-transfer reactions. To approach the opposite limit of removing/depositing an isolated adatom on the (100) surface, we report the case of a corrosion from a perfect (100) surface. Corrosion from the perfect single-crystal surface should correspond to the most difficult nucleation bottleneck, and we expect far less favorable thermodynamics and kinetics. The results, at 1.00 V vs. SHE, in Figure 3.3, shows the optimized free energy curve for the single constraint of fixed vertical displacement of one tagged atom, at 1.00 V vs. SHE, and the associated optimized value of the displacement in the plane of the surface. Figure 3.3 reveals the existence of two possible pathways to create this defect. The first one forms a vacancy-adatom pair structure (*defect-formation pathway*, as illustrated by bottom inset of Figure 3.3) from which the adatom subsequently corrodes. In the second pathway, a top layer Ag atom escapes directly into solution (*vertical pathway*) through a bridging structure formed by the waters over the hole. Based on the free energy profile, the *defect-formation pathway* will be less difficult.

We next consider the bias dependence of the two elementary steps associated with the defect-formation pathway, as shown in Figure 3.4. Two activation barriers are obtained. The first one occurs 1.5 Å above the top layer of the surface (blue region, deformation step) where the vacancy-adatom pair is formed (pink region), accessing a local minimum at about 2 Å. This first barrier is only weakly dependent on the applied potential, suggesting that the vacancy-adatom pair formation

is governed more by local chemical interaction between metal atoms. This is supported by the fact that the partial charge in the adatom complex is largely insensitive to the applied voltage. The second activation barrier occurs at approximately 3.5 Å above the surface layer (yellow region: adatom detachment regime). This second barrier depends much more strongly on applied bias than the first barrier, and exhibits a free energy profile similar to the adatom corrosion case shown previously in Figure 3.1. Therefore, it can be suggested that electrochemically observable corrosion is initiated from already roughened surfaces. This is reinforced by the fact that predicted thermodynamics are unfavorable for creation of the adatom defect at 1.00 V in perfect Ag(100) based on the calculations (higher biases change this balance). Partial solvation of the newly created adatom does not fully compensate for its reduced metal-metal bonding strength, even at 1.00 V. Nucleating this defect is a bottleneck, as the chemical process of breaking the bonds of a top layer Ag(100) atom to reform as an adatom are only slightly stabilized by applied bias. Nonetheless, the drop in barrier from 0.75 eV (at 0.00 V) to 0.6 eV (at 1.00 V) makes this nucleation step possible at room temperature. The 298 K turnover frequency associated with these two barriers (calculated through transition state theory) are 1.3 sec^{-1} and $4.4 \times 10^2 \text{ sec}^{-1}$ respectively.

The partial charge analysis shown in Figure 3.4 provides interesting data on the role of charge flow in the electrode as a function of Ag atom displacement away from the surface (and as a function of applied bias). The top right plot (Fig. 3.4b) reveals the generation of the Ag cation as well as some striking effects in the net charge of the remaining surface atoms (“bulk charge”). At low biases, the bulk shows a marked loss of net positive charge at around $z = 1.4 \text{ Å}$ as the barrier to adatom formation is crossed. We associate this with the induction of a negative “image”-like charge in the surface layer atoms adjoining the partially positively charged adatom (as previously highlighted in Figure 3.2) that helps to stabilize the adatom against oxidation. As before, this formation of “image”-like charge is attenuated at higher biases, which synergizes with weakened metal-metal bonding at higher biases to make corrosion more favorable. Notably, the “image”-like interaction is more strongly manifested in the defect-formation pathway compared to the vertical formation pathway. The comparison of this potential-dependent partial charges for both pathways is shown in Sec. C.3.1.

3.4 Conclusions

The durability of electrochemical devices presents a challenge that basic science can contribute to by enhancing our knowledge of the elementary steps associated with corrosion and deposition. Despite numerous previous studies, there still exists knowledge gaps even for a relatively simple system, such as metallic silver electrodes. In particular, to our knowledge, there have been no previous simulations of the bias-dependence of elementary reaction steps such as adatom corrosion/deposition, or the nucleation of a defect site from which subsequent corrosion will be facile. Equally surprising, there are no existing experimental measurements of the ion-transfer kinetics associated with corrosion and deposition that are cleanly separated from other co-existing processes such as nucleation.

We have reported a computational study on silver that fills some of these gaps. On the simulation side, we report the application of density functional theory (DFT) with applied bias, coupled with

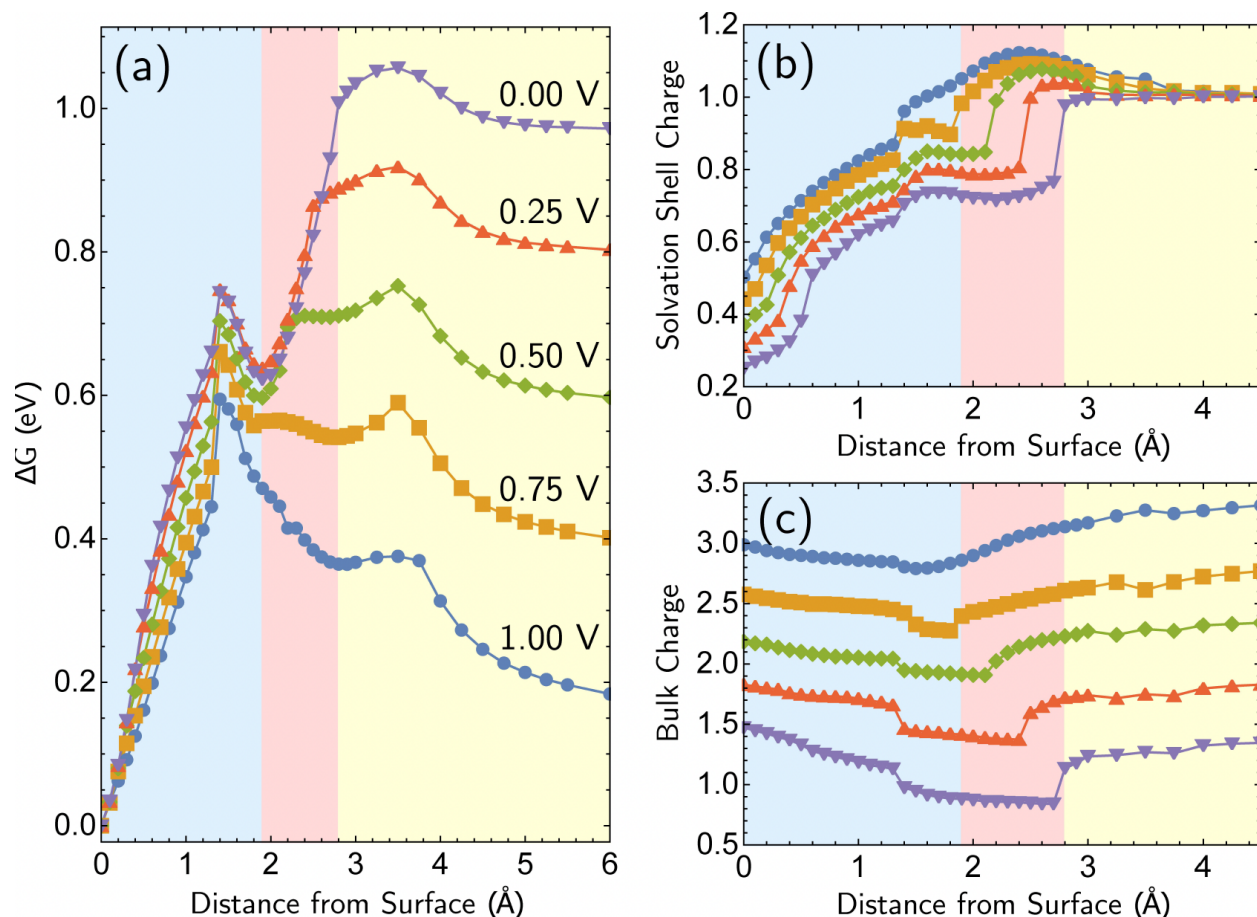


Figure 3.4: Free energy curves and charge profiles for the *defect-formation* pathway for Ag^+ formation from perfectly $\text{Ag}(100)$. The region approximately between 0 $\text{\AA}$ to 2 $\text{\AA}$ denotes the deformation step (blue background), 2 $\text{\AA}$ to 3 $\text{\AA}$ the detachment step (pink background), and beyond 3 $\text{\AA}$ is the adatom corrosion step (yellow background). (a) Free energy curves for the *defect-formation* pathway as a function of applied bias. (b-c) Solvation shell and bulk partial charges as a function of bias for the *defect-formation* pathway. The sum of two partial charges is equal to the total charge of the cell for each data point.

a mixed explicit/implicit solvent model and continuum electrolyte to explore corrosion/deposition on an $\text{Ag}(100)$ surface. This is an advanced model in terms of correctly including the progressive charge depletion associated with the electrode under positive bias, and yielding bias-dependent values for the free energy change for atom corrosion/deposition (Eq. (3.1)), and its associated barrier.

A few of our key results are as follows. For the case of a single adatom on a perfect surface corroding to Ag^+ , the calculated equilibrium potential vs SHE is 0.68 V, with a corresponding kinetic barrier of 0.21 eV, and transfer coefficient of 0.54. Good qualitative agreement was observed with

our newly obtained experimental values of 0.38 eV for the kinetic barrier, and a transfer coefficient of 0.4, which serves to broadly validate the simulation approach. Thus validated, analysis of adatom charge and solvation from the simulations as a function of vertical displacement and applied voltage give insight into the factors promoting corrosion at high positive bias. In brief, these are weakened metal-metal bonding as seen in more positive adatom charge, as well as the inability to develop a stabilizing image charge as occurs at low biases, together with partial solvation of the emerging ion. Simulations were also reported for the case of generating a defect in an otherwise perfect Ag(100) surface corresponds to a slow nucleation step: the thermodynamics are calculated to be unfavorable even at +1.00 V, and the kinetic barrier is around 0.6 V. The optimal calculated path corresponds to generating a defect-adatom pair, followed by loss of the adatom to solution as an ion. The underlying physical reasons were analyzed. Both the simulation and experimental approach used here can be usefully extended to more heterogeneous and complex processes such as bivalent metal corrosion/deposition, electrolyte and solvent effects, corrosion-related processes at cathodes and more, with substantial opportunity for new insights.

We note that the reported simulation is highly simplified in terms of accounting only for the minimum explicit solvation needed to account for the hydration energy of Ag^+ , with all remaining solvent and electrolyte effects were captured implicitly. Therefore, the simulations omit entropic effects associated with solvent/electrode dynamics. Experimental validation was therefore crucial, and was provided by new measurements performed by our collaborators. In brief, the experimental model quantified the kinetics of ion-transfer at the electrode interface in the absence of nucleation via the use of electrodes comprised of 2 nm Ag clusters deposited on gold. The full details on the experimental portion of this work is available in the published journal article Ref. [447].

Supporting Information

Original versions of both main text and the Supporting Information can be accessed in the online published version of Ref. [447]. which contains full data table containing computed values as well as geometry files used in this work. The article is open access.

Chapter 4

On the Role of Hydroxide Ions as the Mediators of Cathodic Copper Corrosion

4.1 Introduction

While anodic corrosion has been extensively studied, cathodic corrosion [448–450] has received minimal attention in the literature until recently. Though it was first observed in 1898 by Fritz Haber, [451, 452] cathodic corrosion was largely ignored for decades, until interest revived in the early 2010s as part of developing a toolkit for colloidal nanoparticle synthesis. [448, 449, 453–456] Cathodic corrosion might at first glance appear to be a contradiction because reductive processes should normally be responsible for deposition rather than dissolution. This still rather enigmatic term nowadays refers to all irreversible structural changes, ranging from surface transformations and roughening, to dissolution, that occur at the negatively biased metal-solution interface. [450]

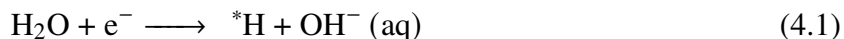
Advances in *operando* experimental techniques have played a pivotal role in renewing interest in dynamic restructuring of cathodes. The onset potentials of cathodic corrosion for metals are moderately negative (e.g. -1.3 V vs. Normal Hydrogen Electrode (NHE) for Pt) [457]. The hydrogen evolution reaction (HER) is highly active at this potential, challenging accurate experimental measurements. Recent progress in microscopy and spectroscopy, however, allows real time observation of the cathodic surface. For example, liquid-cell transmission electron microscopy (TEM) has been used to report dynamic evolution of Pt nanoparticles formed in cathodic corrosion. [458]

Our present focus is on irreversible chemical transformations occurring on cathodic copper electrodes. This topic is of interest due to copper's key role in carbon dioxide reduction reactions (CO₂RR). [459, 460] Numerous studies have reported surface restructuring of Cu under CO₂RR conditions using various *operando* imaging techniques, such as atomic force microscopy (AFM) [461–463], scanning tunneling microscopy (STM) [464], scanning electron microscopy (SEM) [465–467], and liquid-cell TEM (TEM). [468–472] Notably, a distinct amorphous phase at the metal-solution interface has been reported through liquid-cell TEM. [473] Novel spectroscopic tools such as *operando* Raman, surface X-ray diffraction, and X-ray absorption spectroscopy (XAS)

have also been used to identify intermediates that can generate exposed Cu (and Pt) sites. [461, 464, 468, 471, 474–476]

Computational studies have also yielded insights on elementary steps that govern the durability. Computed Pourbaix diagrams have offered a traditional thermodynamic view of cathodic stability. [477–481] Advances in constant potential models (beyond the Computational Hydrogen Electrode (CHE) [11]) have further enabled improved modeling of the cathodic environment. For example, grand canonical density functional theory (GC-DFT) [235, 242, 243] coupled with genetic algorithms [17, 18, 20] for conformational searches have allowed accurate exploration of chemical space. This approach has been used to identify the role of CO₂RR intermediates in the restructuring and dissolution of Cu, [482–484] as well as the hydrogen-induced restructuring of Cu(100). [485, 486] Constant potential force fields and constant Fermi-level molecular dynamics have also been developed and utilized to study cathodic corrosion. [246, 247, 487, 488]

Despite important progress, unanswered questions remain concerning the nature of cathodic corrosion at Cu. Specifically, the role of hydroxide ions have been little studied although OH[−] is the dominant byproduct which drives the local pH near the cathode near or above 7. The Volmer reaction, the first step of the hydrogen evolution reaction (HER), proceeds by water electrolysis in alkaline conditions:



Previous work has found that the correct use of this reaction as the proton source (and not the acidic counterpart of Eq. (4.1) starting from H₃O⁺) to be important in computing correct catalytic trends of CO₂RR. [417] Autodissociation of water on Cu(110) has been reported through X-ray photoelectron spectroscopy measurements as well. [489] Pourbaix diagrams of Cu also show aqueous [Cu(OH)₄]^{2−} as a thermodynamically stable phase. [490] All of these suggest that Cu(OH)_{*n*} species can exist in solution, particularly near locally alkaline cathode surface. Indeed, recent evidence suggests that surface hydroxyls play a role in surface restructuring. A computational study based on DFT and kinetic Monte Carlo (kMC) calculations supports surface Cu(OH) as mediators of cathodic corrosion. [491] Experimental data obtained through AFM and Raman, combined with grand-canonical DFT, suggests that hydroxyl-induced metastable active sites can open pathways to restructuring. [492] Apart from hydroxides, other oxygen-involved processes under CO₂RR operating conditions may induce cathodic corrosion, such as diffusion of surface oxygens [237, 493] or repeated cycling between the cathodic operating voltage and open-circuit potentials. [464, 465]

Further exploring the role of Cu(OH)_{*n*}, in particular their formation and potential role in cathodic corrosion, will enrich our understanding of the dynamic Cu interface. With this motivation, we report a computational study evaluating the role of adatom-based Cu(OH)_{*n*} intermediates formed through the alkaline Volmer reaction. We examine their formation and dissolution on Cu(100) using the Constant Electrode Potential (CEP) model. [235, 417, 447] We employ a hybrid solvation model based on implicit description of the solvent/electrolyte and explicit hydrogen bonding between Cu(OH)_{*n*} and the first solvation shell. [447] This model is combined with the CEP protocol to calculate the voltage-dependent energetics of dissolution/deposition of the Cu(OH)_{*n*} complex

adsorbed on Cu(100) surface. Our results show that all $\text{Cu}(\text{OH})_n$ species modeled have Cu(I) oxidation state, which agrees with previous experimental observations. [494] Atomic partial charges reveal the presence of induced quadrupoles and their changes which affect the thermodynamic and kinetic stability of surface complexes. We also quantify the free energy to form $\text{Cu}(\text{OH})_n$ species, as well as the role of surface oxygens that may assist in their formation. These new findings suggest that the transient $\text{Cu}(\text{OH})/[\text{Cu}(\text{OH})_2]^-$ formed from OH^- can trigger structural changes at a cathodic Cu electrode over long timescales.

4.2 Computational Details

Electronic Structure Calculations. Q-Chem v6.1 [335] package was used to design the hybrid solvation model. All structures were optimized with $\omega\text{B97M-V}$ [119] functional with def2-SVPD basis [341, 424], followed by a single-point calculation with def2-TZVPPD. [341, 424] Conductor-like polarizable continuum model was applied as the implicit solvation model. [495, 496] Initial guesses of the solvation shell structures were obtained using the WATER27 database, [422, 423] and placing $\text{Cu}(\text{OH})_n$ at the center of the solvation shell.

Vienna *Ab Initio* Simulation Package (VASP) v6.2.0 [426–429] accelerated through GPU processors was used for all slab calculations, using RPBE density functional [88] with the projector augmented wave (PAW) pseudopotentials. [430] This includes all supercell design, CEP calculations, and the transition state calculations involved for modeling formation of $\text{Cu}(\text{OH})_n$ structures.

To design the supercell, the lattice constant of a cubic Cu fcc cell was computed through a unit cell relaxation on a $12 \times 12 \times 12$ Monkhorst-Pack (MP) grid. [431] The electronic energy and the atomic force were converged to 10^{-6} eV and 10^{-4} eV/Å, respectively. The plane-wave cut-off of 600 eV, and a Gaussian smearing width of 0.05 eV was applied. The resulting lattice constant was 3.680 Å. Using this value, a Cu(100) surface was modeled with 3 layers of 16 Cu atoms a total of Cu atoms. On the topmost layer, a single adatom was placed on a lattice site to model a roughened surface.

The CEP calculations used VASP, VASPsol [418, 419, 432] and Atomic Simulation Environment. [434] The absolute theoretical standard hydrogen electrode (SHE) was set to 4.43 eV for all CEP calculations. [435, 436]. Electrode potential, electronic energy, and the atomic force were converged to 10^{-3} V, 10^{-6} eV, and 0.03 eV/Å, respectively. An MP grid of $4 \times 4 \times 1$ was used for CEP calculations, with plane-wave cut-off and Gaussian smearing width values identical to the previous sections. A linearized implicit solvent/electrolyte of ~ 20 Å was placed between two images in the surface normal direction. A Debye Length of $\kappa_b^{-1} = 9.000$ Å and a dielectric constant of $\epsilon = 78.39$ were used to model a 0.1 M monovalent electrolyte. The cavitation energy was neglected to avoid numerical instabilities. The final CEP free energy was corrected for the finite cell-height. [433] No dispersion corrections were employed, to avoid unphysical overbinding of the corroding atom. [447]

The atomic partial charges were calculated with iterative Hirshfeld (HI) partitioning [437, 438] with the damping function parameter of 1.000. The CEP-optimized structures and the final

number of electrons were used to obtain the HI charges. The converged wavefunctions of the CEP calculations were used.

Modeling Electrodesorption of $\text{Cu}(\text{OH})_n$ Complexes. The initial structure of all $\text{Cu}(\text{OH})_n$ first optimized at $z = 4 \text{ \AA}$ above surface normal, with three explicit waters for $\text{Cu}(\text{OH})$ and five explicit waters for $\text{Cu}(\text{OH})_2$. Subsequent calculations reduced z repeatedly with the step size of $\delta z = 0.5 \text{ \AA}$, starting from the previous converged result apart from translating the optimized solvation shell structure of $\text{Cu}(\text{OH})_n(\text{H}_2\text{O})_m$ by the step δz to yield a sequence of constrained optimizations. The procedure was reversed when hysteresis was observed to get the lower energy structure. In all cases, the approaching/departing Cu ion within the solvation shell was only allowed to relax in surface parallel direction. All coordinates of all explicit OH, H_2O and the topmost layer of $\text{Cu}(100)$ were left free. All coordinates of the bottom two layers of $\text{Cu}(100)$ were held frozen.

Modeling Formation of $\text{Cu}(\text{OH})_n$ Complexes. To examine the formation of surface-adsorbed $\text{Cu}(\text{OH})_n$ structures, both CEP calculations and transition state search calculations were employed. Due to cost considerations, only -1.59 V vs. SHE was considered. First, the CEP calculations were carried out to optimize initial and final structures of $^*\text{Cu}$, $^*\text{Cu}(\text{OH})$, and $^*\text{Cu}(\text{OH})_2$ adatom structures using 5 explicit water molecules under -1.59 V vs. SHE . When appropriate, the $^*\text{O}$ or $^*\text{OH}$ were placed on the hollow site near the surface adatom and subsequently relaxed under CEP protocol. To optimize the transition state for the formation, both Climbing Image Nudged Elastic Band (CI-NEB) [497] and Dimer Method [498, 499]) were utilized. The transition state was first obtained via CI-NEB. Since CI-NEB cannot be used with CEP, we instead carried out a constant charge CI-NEB using the average number of electrons determined by CEP calculations on the initial and final states. Four images were used for all CI-NEB calculations. The transition states involving surface $^*\text{O}$ or $^*\text{OH}$ required additional refinement with the Dimer method, using the roughly converged CI-NEB result. The final CEP energetics of the converged transition state structures were computed through a single-point CEP calculation, which only iterates the number of electrons to align the Fermi level of the system with -1.59 V vs. SHE without any geometry relaxation.

4.3 Results and Discussion

The operating conditions for the CO_2RR are sufficiently cathodic that the alkaline Volmer reaction (Eq. (4.1)) occurs spontaneously. This creates a non-equilibrium pH gradient away from the electrode, balancing OH^- production and the rate of transport. During its residence time close to the electrode, the OH^- produced via Eq. (4.1) can interact or react with nearby reactive surface features or terraces characteristic of roughened surfaces. We propose that such interactions can lead to formation of $\text{Cu}(\text{OH})$ or $\text{Cu}(\text{OH})_2$ adsorbates (Fig. 4.1). To test this hypothesis, we have subsequently focused on computing voltage-dependent free energies of these complexes relative to the reactants.

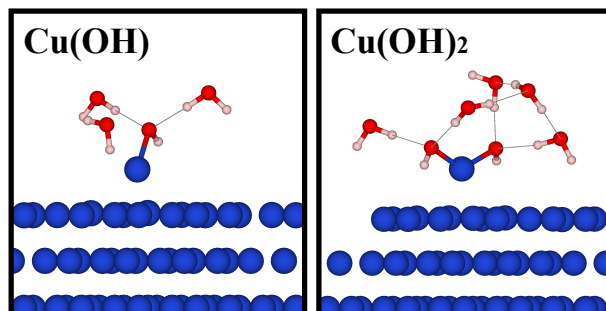


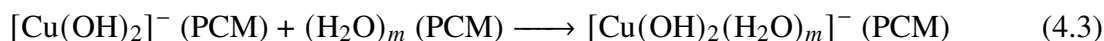
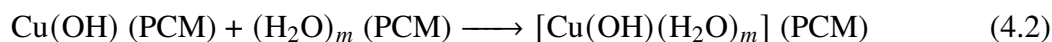
Figure 4.1: Schematic of Cu(OH) and Cu(OH)_2 complexes formed around an adatom on Cu(100) surface. Each complex is solvated with three and five explicit H_2O water molecules atop of a linearized Poisson-Boltzmann implicit solution, latter of which is not shown in the schematic.

4.3.1 Design of the Hybrid Solvation Model

No. of explicit H_2O (m)	1	2	3	4	5	6
$\Delta\Delta E_{\text{solv},m}^{\text{CuOH}}$ (eV)	0.97	1.10	1.20	1.08	1.17	1.07
$\Delta\Delta E_{\text{solv},m}^{[\text{Cu(OH)}_2]^-}$ (eV)	0.31	0.48	0.60	0.58	0.75	0.93

Table 4.1: Explicit hydration energy $\Delta\Delta E_{\text{solv}}$ with m explicit H_2O molecules.

Our previous work has shown that a purely implicit description of the solvation of a nascent metal ion does not provide adequate stabilization, due primarily to its neglect of explicit strong interactions in the first solvent shell. [447] We addressed this deficiency by designing a computationally efficient hybrid solvation model that uses a minimal number of explicit solvent molecules in addition to implicit solvation. In brief, we consider $\Delta\Delta E_{\text{solv}}$ versus m , the change in ion solvation energy as a function of m , the number of explicit solvent molecules included. The smallest value of m to saturate $\Delta\Delta E_{\text{solv}}$ is then chosen. For Cu(OH) and $[\text{Cu(OH)}_2]^-$, $\Delta\Delta E_{\text{solv}}$ will be determined through



where PCM refers to the Polarizable Continuum Model (PCM). [420, 421] This approach can in principle be generalized to any type of solvent and solute. The results of these calculations are shown in Table 4.1. The value of $\Delta\Delta E_{\text{solv}}$ is sufficiently converged after three explicit waters for Cu(OH) and five for $[\text{Cu(OH)}_2]^-$, leading us to choose $m = 3$ and $m = 5$ for these two complexes. Explicit waters coordinated to the hydroxide ions provide the most stabilization.

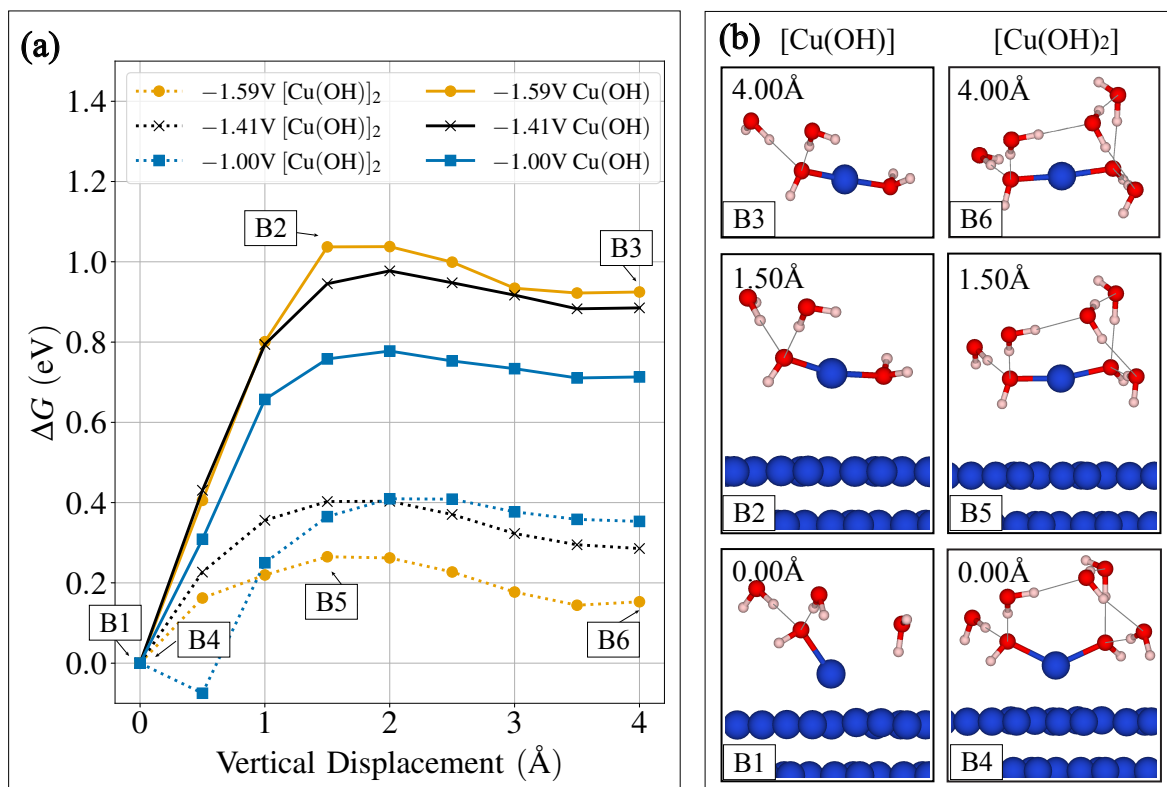


Figure 4.2: Free energy profile of the electrodisolution of Cu(OH)_n adatom complexes. (a) Voltage-dependent free energy surfaces for electrodisolution of Cu(OH)_n . (b) Adatom structures relaxed at -1.59 V along vertical displacement. Corresponding points at free energy surfaces are denoted.

4.3.2 Electrodisolution of Cu(OH)_n Adatom Complexes

We first study the dissolution of Cu(OH) and Cu(OH)_2 complexes formed on an electrode adatom, which is the most reactive metal atom due to its undercoordination. Using a sequence of constrained CEP geometry optimization, we computed potential-dependent free energy surfaces for the vertical displacement of the adatom chaperoned by its explicit water molecules. A total of three potentials were explored, -1.59 V, -1.41 V, and -1.00 V vs. SHE (Standard Hydrogen Electrode). The first two potentials are equivalent to -1.00 V vs. RHE (Reversible Hydrogen Electrode) at $\text{pH} = 10$ and $\text{pH} = 7$ at room temperature, respectively.

Fig. 4.2a shows the simulation results of the bias-dependent free energy profiles for Cu(OH) and Cu(OH)_2 as a function of displacement, z , from the Cu(100) surface. Illustrations of the resulting optimized structures at selected data points for -1.59 V vs. SHE are shown in Fig. 4.2b. First, the thermodynamics show that the dissolution of Cu(OH) (i.e. the large z limit) is endergonic for all three voltages. The fully dissolved structure ($z = 4.00$ Å) is 0.75 eV higher in free energy than the surface-bound structure ($z = 0.00$ Å) at -1.00 V vs. SHE. This energy difference increases to 0.93

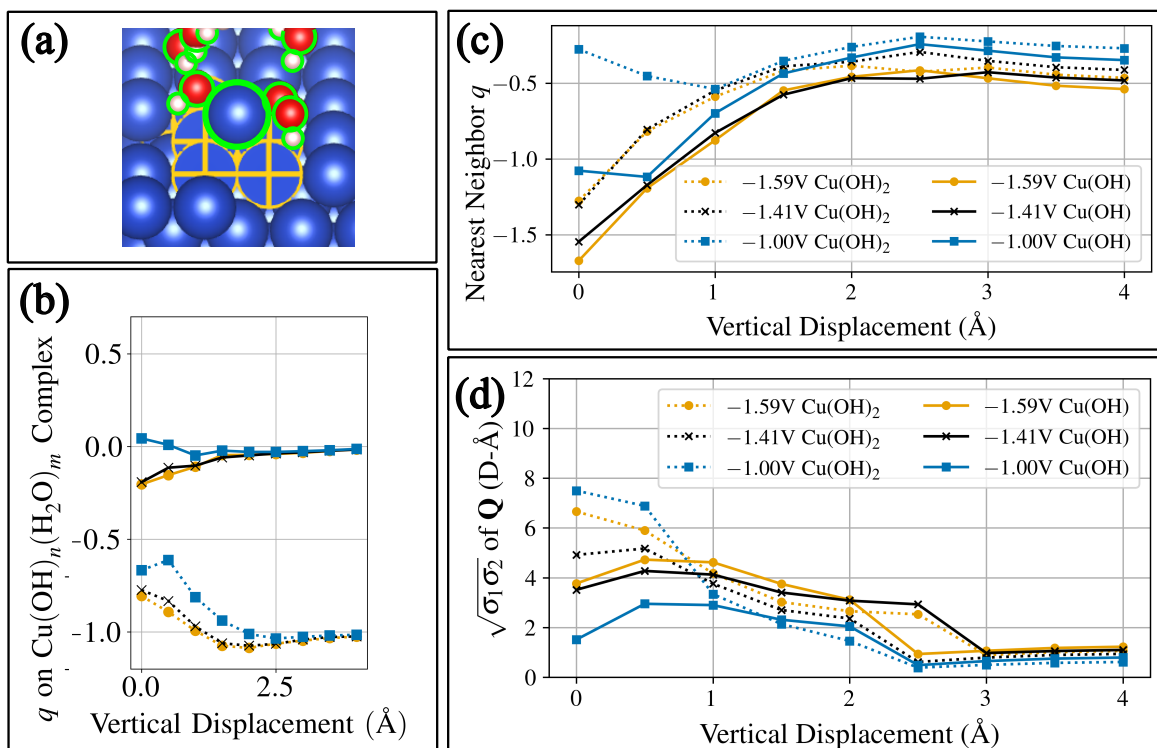


Figure 4.3: Atomic partial charges localized around $\text{Cu}(\text{OH})_n(\text{H}_2\text{O})_m$. (a) Schematic of the subsystems analyzed. Surface Cu atoms (blue) with yellow contours are the nearest neighbor atoms. Adatom Cu, oxygens (red) and hydrogen (white) with lime green contour correspond to the adatom complex and its first explicit solvation shell. Figures (b-d) show the changes in three quantities with respect to the vertical displacement of the adatom complex – (b) the sum of partial charges q on the dissolving complex including explicit waters, (c) the sum of partial charges q on surface atoms that are nearest neighbors of the adatom complex, and (d) the geometric mean of the two singular values σ_1, σ_2 of the quadrupole tensor, $\mathbf{Q}$, associated with charges on the nearest neighbor surface atoms.

eV under -1.59 V vs. SHE: more cathodic potentials require more free energy to dissolve $\text{Cu}(\text{OH})$ from the surface.

Switching to kinetics, the calculated barrier to detach the complex from the surface ($\Delta G^\ddagger$) is also not small: it requires 0.84 eV at -1.00 V vs. SHE and 1.04 eV at -1.59 V vs. SHE. The rate constant k estimated at room temperature (298 K) using computed $\Delta G^\ddagger$ and transition state theory (TST) are $1.78 \times 10^{-5} \text{ s}^{-1}$, $1.87 \times 10^{-4} \text{ s}^{-1}$ and $4.44 \times 10^{-1} \text{ s}^{-1}$ for -1.59 V, -1.41 V, and -1.00 V respectively. Thus electrodisolution of $\text{Cu}(\text{OH})$ is ~ 25000 times more likely at -1.00 V compared to -1.59 V.

Some insight into the high energetic cost and large barriers calculated for the dissolution of $\text{Cu}(\text{OH})$ can be obtained from examination of partial charges localized on the complexes (high-

lighted with lime green in Fig. 4.3a). The $\text{Cu}(\text{OH})$ complex remains essentially neutral as a function of z for all simulated potentials (solid lines on Fig. 4.3b). Detaching a neutral species from a negatively charged electrode surface must occur without any electrostatic driving force at long range. The cost of making small displacements (from 0 to 1.5 Å) is responsible for most of the energetic cost. Evidently local polarization of surface atoms to stabilize surface-bound $\text{Cu}(\text{I})\text{OH}^{\delta-}$ increases with more cathodic potentials, and must be overcome to approach the displacement corresponding to the transition state structure (~ 1.5 Å; Fig. 4.2). Therefore more cathodic potentials will result in increasingly strongly bound $\text{Cu}(\text{OH})$ species.

By contrast, dissolution of a $\text{Cu}(\text{OH})_2$ complex is much less unfavorable. Fig. 4.2a also shows the free energy profiles for the dissolution/deposition of $\text{Cu}(\text{OH})_2$. Dissolution is far less endergonic for all three simulated potentials, and we see a significant drop in the energy barriers relative to those of $\text{Cu}(\text{OH})$ complex. For -1.59 V vs. SHE, $\Delta G^\ddagger$ is reduced four-fold from 1.04 eV to 0.27 eV with an additional OH^- ion. In addition, a more cathodic potential makes dissolution easier, and reduces the barrier, which is the opposite of the case of $\text{Cu}(\text{OH})$. The estimated rate constant k are $2.05 \times 10^8 \text{ s}^{-1}$, $9.42 \times 10^5 \text{ s}^{-1}$ and $7.42 \times 10^5 \text{ s}^{-1}$, for -1.59 V, -1.41 V, and -1.00 V respectively. This shows that *operando* Cu electrodisolution through formation of surface-bound $\text{Cu}(\text{OH})_2$ is quite facile, presuming that complex can be formed (see following section).

The reversal of the trend can again be explained through the partial charges on the $\text{Cu}(\text{OH})_2$ complex (dashed lines, Fig. 4.3b) Unlike the case of $\text{Cu}(\text{OH})$, the partial charge localized on $\text{Cu}(\text{OH})_2$ is negative, with $q \leq -0.6$ for all voltages explored and approaching -1 at the dissociation limit. Importantly, the undissolved complex already is negatively charged. This renders the electrostatic interaction between the electrode and the surface complex fundamentally repulsive. Therefore, as the Cu is more cathodically polarized, the adatom $\text{Cu}(\text{OH})_2$ complex can more easily escape the surface. This result also agrees with Ref. [450] in that an anionic intermediate facilitates the cathodic corrosion.

What is the chemical nature of the Cu adatom complex? In particular, what is the oxidation state of the Cu in the dissolving complex? Fig. 4.3b strongly suggest that the copper adatoms are oxidized as Cu(I) in both the $\text{Cu}(\text{OH})_2^-$ and $\text{Cu}(\text{OH})$ complexes. It is interesting and surprising that the Cu adatom, the oxidation state only minimally varies as a function of z . For $\text{Cu}(\text{OH})$ at -1.59 V vs. SHE, the partial charge of the complex is $q = -0.204$ for the chemisorbed structure ($z = 0.00$ Å) versus $q = -0.016$ for the dissolved structure ($z = 4.00$ Å). Under the same bias, the chemisorbed $\text{Cu}(\text{OH})_2$ complex has a net charge of $q = -0.806$ versus $q = -1.025$ for the dissolved structure. In other words, the Cu adatom is pre-oxidized as Cu(I) in the surface-bound complexes despite the cathode being biased quite strongly negative. We note that a few experimental studies have already proposed Cu^+ species as potential intermediates that can drive restructuring. [473, 500]

We now examine the local charge distribution surrounding the adatom complex, focusing on the nearest neighbor atoms that are in direct coordination with the adatom at the surface-bound geometry (highlighted with yellow solid lines in Fig. 4.3a). To quantify this, the total charge q and the quadrupole Q produced by the nearest neighbors are analyzed with respect to voltage and vertical displacement of the adatom. Since this subsystem can carry a non-zero net charge, Q is dependent on the choice of origin. To ensure a proper comparison, we chose the four-fold

hollow site directly below the adatom as the origin for all displacement values. Figs. 4.3c and 4.3d compare total q and the geometric mean of the singular values of $\mathbf{Q}$. The summed charges show that for both complexes and under all potentials, nearest neighbors hold net negative charges. Applying more negative biases also increases the magnitude of the total charge on this subsystem. However, as might be anticipated, the nearest neighbors hold slightly less negative charge for $\text{Cu}(\text{OH})_2$ compared to $\text{Cu}(\text{OH})$ (Fig. 4.3c). The polarization of charges across the four atoms also increases for $\text{Cu}(\text{OH})_2$, demonstrated by the increased geometric mean of the singular values of $\mathbf{Q}$ tensor (Fig. 4.3d).

A closer examination of the atomic charges localized on each atom reveals a crucial insight into the image multipoles, which explains both increased surface polarization and thermodynamics of dissolution. Fig. 4.4 presents a schematic of the two representative cases of surface-bound $^*\text{Cu}(\text{OH})$ and $^*\text{Cu}(\text{OH})_2$. The left panels confirm the monopole-monopole interaction picture between the $\text{Cu}(\text{OH})_n$ and the nearest neighbor atoms: increased repulsive interaction between the nearest neighbors and the adatom complex makes the dissolution of $^*\text{Cu}(\text{OH})_2$ easier than $^*\text{Cu}(\text{OH})$. The right panels however show that the surface charge distributions of the two are qualitatively different. All four nearest neighbor atoms in the undisplaced $^*\text{Cu}(\text{OH})$ structure under are partially reduced as a result of an image charge response to the partially oxidized adatom atop. The attractive interaction between the nearest neighbor atoms and the adatom complex is thus a monopole-monopole interaction, whose strength decays as $\sim 1/r$ and keeps the structure thermodynamically stable. This attractive interaction however is disrupted once H_2O directly coordinates to the adatom Cu. While this requires a significant increase in the free energy, it alters the homogeneous image charge distribution on the nearest neighbor atoms and weakens the stabilization. (Fig. Fig. 4.5).

In contrast, two of the four nearest neighbors of the undisplaced $\text{Cu}(\text{OH})_2$ structure are partially oxidized ($\text{Cu}^{\delta+}$), which is an image charge response to the two opposing dipoles of hydroxyls lying close to the surface plane. The oscillation of charges is in fact present beyond the nearest neighbor atoms, generating a locally ionic character. The attractive interaction between the nearest neighbor atoms and the adatom complex is thus a quadrupole-quadrupole interaction, whose strength decays as $\sim 1/r^5$. Therefore, the weaker attractive force between the surface complex and the nearest neighbor atoms allows more facile dissociation of $\text{Cu}(\text{OH})_2$.

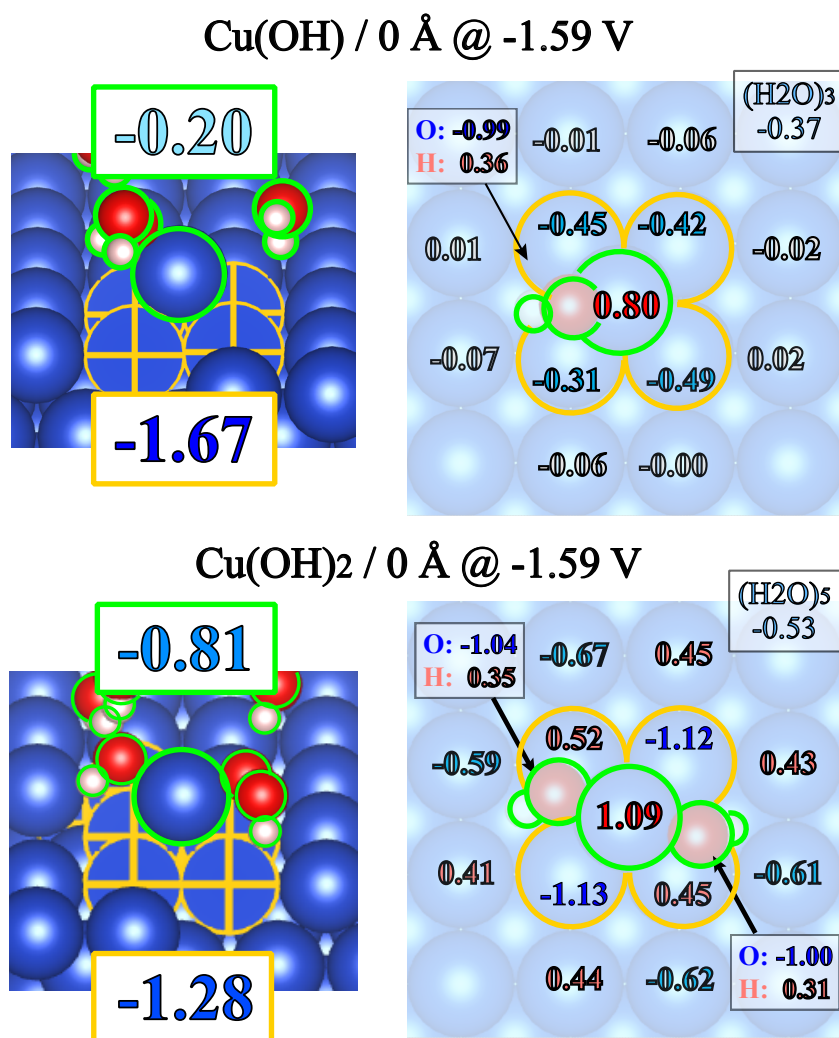


Figure 4.4: Schematic of the image interaction between surface complex and the nearest neighbor atoms for Cu(OH) and Cu(OH)₂ complexes under -1.59 V vs. SHE. On the left panel, the sum of charges localized on Cu(OH)_n (including the explicit waters) and the sum of the charges on the four nearest neighbor atoms are highlighted with lime green and yellow, respectively. On the right panel, top view of the partial charges on the surface atoms are visualized and color-coded (red-to-blue) by sign. Explicit waters have not been noted in this panel for clarity, but the total charges on (H₂O)_n are indicated at the top right corner.

4.3.3 Surface Cu(OH) and Cu(OH)₂ Formation: A Key Role for *O?

We next assess the formation of surface-bound Cu(OH) and Cu(OH)₂ through the alkaline Volmer reaction Eq.(4.1). We investigate the sequential formation of *Cu(OH) and *Cu(OH)₂, represented

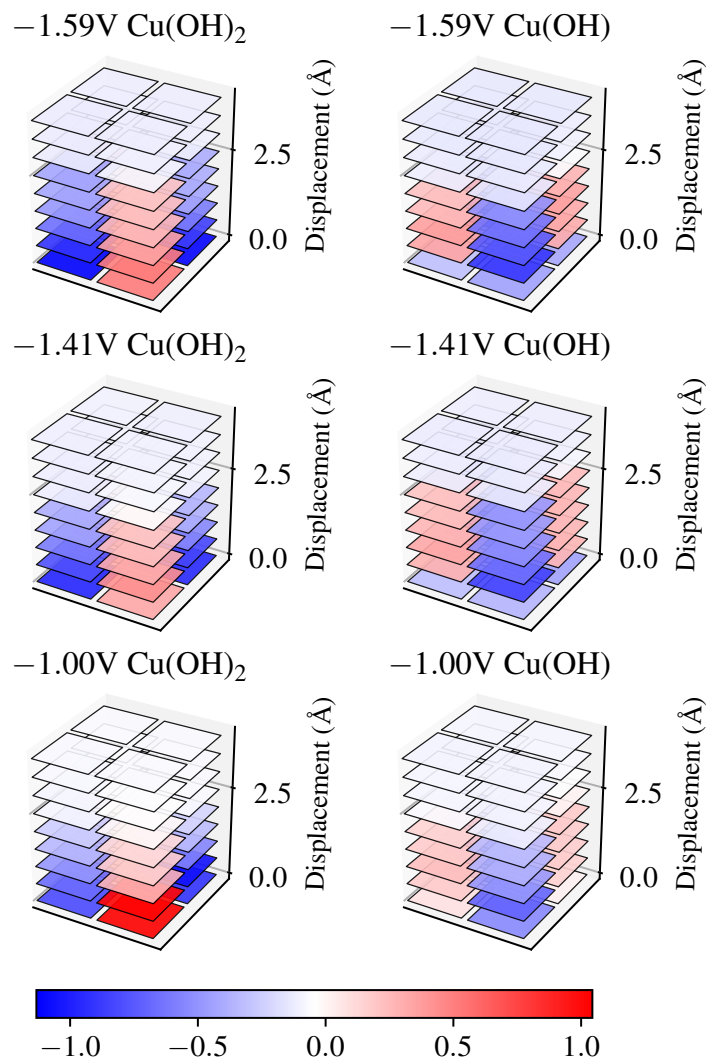
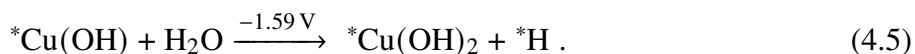
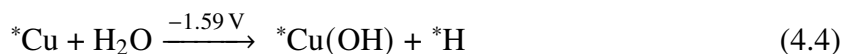


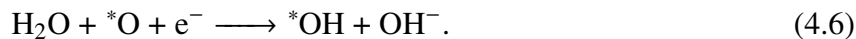
Figure 4.5: Evolution of atomic partial charges as a function of Cu(OH)_n complex displacement. The plots illustrate the charge redistribution on the nearest neighbor atoms for Cu(OH)_2 (left column) and Cu(OH) (right column) at three distinct applied potentials: -1.59 V, -1.41 V, and -1.00 V vs. SHE. One layer (consisting of four co-planar squares) represents the charge distribution on the nearest neighbor atoms, and one square on each layer represent the partial charge on a single nearest neighbor atom. The vertical axis represents the vertical displacement of the adatom complex from its equilibrium undisplaced structure. Partial charges are mapped on a red-to-blue scale.

by:

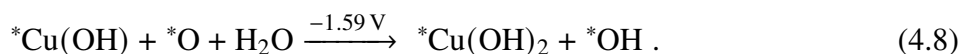
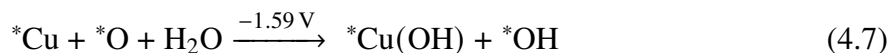


Thermodynamics and kinetics, as well as other properties of the adsorbed complexes, will be determined by the cathodic applied bias, which we chose to be -1.59 V. We do not consider the concerted formation of $\text{Cu}(\text{OH})_2$ (i.e., two H_2O interacting with the Cu adatom simultaneously to form $^*\text{Cu}(\text{OH})_2$ from $^*\text{Cu}$), as simultaneous dissociation of two H_2O molecules with a single Cu adatom is unlikely.

Motivated by literature that suggest the presence of subsurface oxygen and its diffusion to the surface during CO_2RR , [237, 493] we also explored adatom complex formation assisted by the presence of nearby $^*\text{O}$. Given that CO_2RR catalysts are often exposed to repeated cycles of cathodic and open circuit conditions, we hypothesized that $^*\text{O}$ introduced under open circuit conditions (as either Cu_2O or CuO) may assist the formation of adatom complexes and contribute to the experimentally observed surface instability. [464, 465] $^*\text{O}$ may facilitate the alkaline Volmer reaction by generating two hydroxides through dissociative chemisorption:



With the presence of undercoordinated Cu nearby (for instance, an adatom, $^*\text{Cu}$), this leads to the formation of these complexes through an alternative pathway:



To compare the kinetics and the thermodynamics of the two pathways, we used both CEP and transition state search calculations (Climbing Image Nudged Elastic Band [497, 501] (CI-NEB) and the dimer method [498, 499]) to explore the free energies with five explicit water molecules solvating the adatom.

Fig. 4.6a compares the two pathways to form $^*\text{Cu}(\text{OH})$ through Eq. (4.4) and Eq. (4.7). The result shows that $\text{Cu}(\text{OH})$ is much more easily formed with the participation of $^*\text{O}$. Without $^*\text{O}$ nearby, $^*\text{Cu}(\text{OH})$ is only -0.04 eV more stable than reactants, and the barrier is approximately ~ 1 eV, indicating that this reaction is slow. With the $^*\text{O}$ participation, the barrier height is reduced by $\sim 50\%$ and the final structure is > 0.5 eV more stable than the reactants. The rate constant k for both pathways with and without surface oxygen are $7.06 \times 10^4 \text{ s}^{-1}$ and $1.75 \times 10^{-3} \text{ s}^{-1}$, demonstrating ~ 7 orders of magnitude difference. We also note that the energy barrier for the reverse reactions to detach the hydroxide ion is also quite high, requiring at least ≈ 0.7 eV. This means that the Cu adatom complex will be moderately long-lived, once formed by a rare event fluctuation, and thus could have a steady-state concentration.

Next we apply the same analysis to the formation of $^*\text{Cu}(\text{OH})_2$ from $^*\text{Cu}(\text{OH})$. Fig. 4.6b summarizes the comparative free energy landscapes of these two pathways at -1.59 V vs. SHE. The role of $^*\text{O}$ is also unmistakable here. Without $^*\text{O}$ participation, forming $^*\text{Cu}(\text{OH})_2$ from $^*\text{Cu}(\text{OH})$ is even slightly more difficult than forming $^*\text{Cu}(\text{OH})$ itself, with very unfavorable thermodynamics. In striking contrast, $^*\text{O}$ participation dramatically reduces the barrier height by $\sim 80\%$, a drop which is considerably more substantial than that for $\text{Cu}(\text{OH})$ formation. The much more favorable kinetics for associated with surface $^*\text{O}$ for forming both $^*\text{Cu}(\text{OH})$ and $^*\text{Cu}(\text{OH})_2$ reflects two

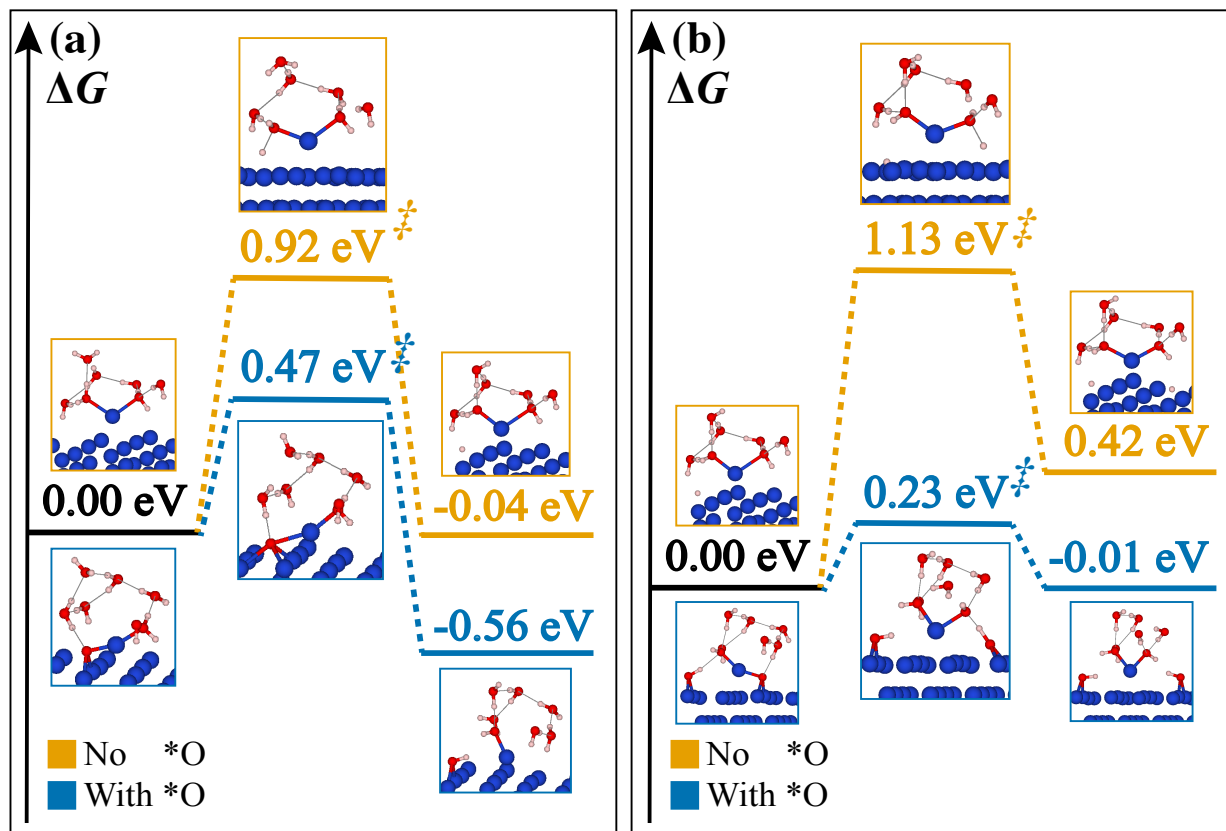


Figure 4.6: Thermodynamic profile of the formation of $^*\text{Cu}(\text{OH})$ and $^*\text{Cu}(\text{OH})_2$ under -1.59 V vs. SHE. Orange bars represent reactions *without* the participation of subsurface oxygen, and the dark blue bars represent reactions with them. The inset images correspond to the optimized initial state, the transition state, and the final state of each pathway from left to right. The transition state is denoted with a double dagger. (a) Formation of $\text{Cu}(\text{OH})$ through two pathways Eq. (4.4) and Eq. (4.7). (b) Formation of $\text{Cu}(\text{OH})_2$ through two pathways Eq. (4.5) and Eq. (4.8).

factors: primarily the proton affinity of $^*\text{O}$ and second the cathodic conditions whereby $^*\text{O}$ binds more strongly to the adatom as it preoxidizes to $\text{Cu}(\text{I})$ than to slightly reduced first layer Cu atoms.

Based on the simulation results, we propose that cathodic corrosion of Cu under CO_2RR operating conditions can occur through following steps:

1. Surface fluctuation causes an adatom site to become generated, which will be locally oxidized. The oxidation state of the copper atom is approximately Cu^+ .
2. Once the copper electrode is biased negative, the vigorous alkaline Volmer reaction causes surface adatoms to interact with OH^- formed at the surface through dissociative chemisorption and form $^*\text{Cu}(\text{OH})$. If the copper catalyst contains $^*\text{O}$, it strongly facilitates $^*\text{Cu}(\text{OH})_2$

formation. Electrodes that are OD-Cu or have been exposed to an open circuit potential may be in this class.

3. Surface-adsorbed $^*\text{Cu}(\text{OH})$ reaches a steady state concentration. Once $^*\text{Cu}(\text{OH})_2$ is formed through an additional alkaline Volmer reaction, it readily dissolves away from the surface, leading to materials loss and potentially surface restructuring, particularly if the electrode material is disordered with a significant concentration of undercoordinated Cu atoms. The final dissolved species is $[\text{Cu}(\text{OH})_2]^-$ with the copper oxidation state of +1.

4.4 Conclusion

In this work, we explored the possible consequences of the alkaline Volmer reaction at the cathode being an abundant source of hydroxide ions, which open pathways to form interfacial copper hydroxides that can dissolve away at the cathode. We computed the electrode potential-dependent free energies of the dissolution of a surface adatom complex using constant electrode potential (CEP) DFT calculations. The results showed that dissolution of $[\text{Cu}(\text{OH})_2]^-$ is much more facile than $\text{Cu}(\text{OH})$. The trend was explained in terms of the electrostatics and the partial charge localized on the surface complex. We also identified the presence of two different image charge responses between surface $\text{Cu}(\text{OH})$ and $\text{Cu}(\text{OH})_2$, resulting in very different electrostatic interactions between the nearest neighbors and the adatom complexes. We then assessed the thermodynamics and kinetics of the formation of the adatom complex using CEP-DFT calculations with transition state searches. We also explored the role of surface oxygen atom participation in facilitating formation of $^*\text{Cu}(\text{OH})$ and $^*\text{Cu}(\text{OH})_2$. The results reveal that the $^*\text{O}$ -mediated pathway is far more facile, although there is no studied reaction to regenerate the $^*\text{O}$ under *operando* conditions.

Our findings differ from earlier works in several aspects. To our knowledge, this is the first work that utilized constant-potential DFT to investigate the mechanism of cathodic Cu corrosion without any involvement of electrolytes. Our proposed mechanism differs from previous works such as Refs [464, 471, 484] as no active involvement of electrolyte-derived intermediates such as CO are formed. Our work also differs from Ref. [491] which also explored Cu–OH but focuses on OD–Cu or copper oxides. Our sources of OH^- ions are the alkaline Volmer reaction and dissociative chemisorption, whereas Ref. [491] primarily considers the hydroxide ions present in the bulk aqueous solution approaching the electrode. In this work, we assumed that the bulk OH^- concentration will be lower than that near the Cu surface, and the unfavorable electrostatics would hinder its approach towards the surface. We also find that there are non-negligible barriers to forming $\text{Cu}(\text{OH})_n$ complexes at the adatom, unlike Ref. [491] which finds no dissolution barrier to uncoordinated atoms.

To end this chapter, we elaborate on the questions that can arise from our results as well as possible experimental/computational studies that can further assess the viability of our proposed mechanism. First, a direct measurement of Cu material loss during CO_2RR operating conditions is needed. Inductively coupled plasma mass spectrometry (ICP-MS) will yield key insights on this front. In fact, this technique has already been used to examine Cu catalyst in the presence of

carbonate electrolyte. [494, 502] We believe that extended experiments using ICP-MS will probe our proposed mechanism. Specifically, comparing material loss with and without CO₂ injection and comparing material loss between pure Cu vs OD-Cu would be helpful in evaluating the viability of our mechanisms. Second, we have proposed the presence of surface oxygen as a potential agent that could facilitate the dissociative chemisorption. This step leaves a spectator hydroxide ion adsorbed to or present nearby the adatom complex. Therefore, any surface spectroscopy that correlates the concentration of surface *OH species with material loss and restructuring will further validate our proposed mechanism, though low concentration or its transient nature may be a challenge in measurement. The surface oxygen is also expected to deplete quite quickly as the metal is exposed to cathodic current. Therefore, a time-resolved ICP-MS measurement that yields dissolution rate change over time will help examine our mechanism. A significant drop in the amount of material loss after a certain time interval can support our surface-oxygen-assisted pathway. The ICP-MS measurements may be combined with operando surface microscopy to obtain a cleaner interpretation of the corrosion mechanism.

Chapter 5

Concluding Remarks

In this dissertation, we have utilized and developed computational quantum chemistry to study physical chemistry of heterogeneous systems. The research was divided into two main thrusts: the development of electronic structure methods for core-electronic ionization/excitations and the application of DFT-based electrode modeling to surface degradation and dissolution. In Chapter 2, we combined orbital-optimized density functional theory (OO-DFT), the one-electron exact two component theory (1eX2C) Hamiltonian, and the non-orthogonal quasidegenerate perturbation theory (NO-QDPT) to model core-hole processes that require spin-orbit coupling (SOC). We analyzed the performance of this approach across a broad spectrum of processes requiring SOC, including valence 2P excitations, $L_{2,3}$ ionizations, and M/N-edge processes. This showed that we can achieve semi-quantitative accuracy for $L_{2,3}$ IP of third row main group elements, which improves upon previous DFT-based methods. However, going beyond the first row transition metals requires a more sophisticated treatment. In Chapters 3 and 4, we shifted focus to modeling electrodisolution and deposition occurring under various electrode conditions. We used the constant electrode potential DFT (CEP-DFT) framework in conjunction with a hybrid solvation model as our main tool. This methodology was applied to the electrodisolution of silver (Chapter 3) and the cathodic degradation of copper (Chapter 4). Notably, our works showed the critical role of the first solvation shell and the image charge interactions between the departing species and the immediate nearest neighboring atoms. The magnitude of image charges (or quadrupoles) as well as their formation and disappearance was identified as key factors governing the ion-transfer kinetics in both of these systems. Collectively, these works showed the value of quantum chemistry in simulating and understanding the physical chemistry of heterogeneous catalytic systems.

Works not discussed in this Dissertation

Two published works that have not been discussed in this dissertation deserve a brief highlight. Both of them are related to K-edge core-excitations. We provide a short description of those works here (* indicates equal contribution from authors):

1. Cunha, L. A.*; Hait, D.*; **Kang, R.**; Mao, Y.; Head-Gordon, M. “Relativistic Orbital-

Optimized Density Functional Theory for Accurate Core-Level Spectroscopy.” *J. Phys. Chem. Lett.* 2022, 13, 3438–3449. [194]:

This work explored using orbital-optimized DFT in conjunction with the 1eX2C Hamiltonian that treats the scalar relativistic terms, essentially laying the foundations for the L-edge work presented in Chapter 2 of this dissertation. This OO-DFT/1eX2C approach shows quantitatively accurate performance in predicting K-edge spectra up to the early first row transition metals.

2. Kim, P.*; **Kang, R.***; Carter-Fenk, K.; Wilson, K. R.; Head-Gordon, M.; Ahmed, M. Structural Evidence of Interanionic Hydrogen Bonding in Phosphoric Acid Solutions. *J. Am. Chem. Soc.* 2025, 147, 44916–44925. [503]:

This work applied EA-TDDFT in conjunction with ab initio molecular dynamics to investigate and characterize the presence of inter-anionic hydrogen bonding between two H_2PO_4^- ions. In addition, energy decomposition analysis was employed to identify interactions between the two fragments that allow apparently “anti-electrostatic” bonding to take place.

Perspective on CEP-DFT for Electrocatalysis

In this dissertation, we presented CEP-DFT with hybrid implicit/explicit solvation model as our main approach for modeling interfacial electrochemisry. Like most simulation models for highly complex systems, our approach comes with notable limitations. Here we provide a brief review of the strengths and limitations of CEP-DFT, as well as ways to go beyond CEP-DFT.

Advantages of CEP-DFT. The primary advantage of the CEP-DFT is that it yields a computationally tractable description of the grand-canonical free energy surface as a function of a small number of atomic coordinates. All of the remaining solvent and electrolyte degrees of freedom are treated implicitly. This allows us to avoid the challenges of discovering rare reactive events through dynamics and yet enables us to characterize key features of the bias-dependent free energy surface. The qualitative change of the resulting reaction profiles with respect to varying bias yields a mean-field picture of how the electrochemical process responds to external bias. In addition, CEP-DFT inherits all the strengths of using quantum chemical tools for molecular modeling. For example, the computed electronic charge density can be used to study potential-induced charge flows between the metal substrate and adsorbates. In fact, the works presented in Chapters 3 and 4 extensively analyze this to identify changes in local oxidation character that influence the kinetics and thermodynamics of metal dissolution and deposition. Examining the projected density of states (PDOS) can also reveal how the changes in orbitals affect the underlying strength of the adsorbate-surface bonding.

Limitations of CEP-DFT. The limitations of CEP-DFT generally arise from three sources: the approximate density functional, the implicit treatment of electrolyte, and the neglect of dynamical effects. First, due to the computational cost of modeling under periodic boundary conditions, CEP-DFT often necessitates using semi-local (GGA or mGGA) functionals. As discussed in Sec. 1.2.4,

these functionals can exhibit SIE, which may result in over-delocalization of charge density across subsystems. The extent of SIE can be especially large in CEP-DFT as it allows a non-integer number of electrons by design. [106]. It is therefore recommended to properly characterize the partial charges on subsystems to monitor the extent of this error, and if possible, perform validation against higher accuracy methods (rung 4 and 5 functionals).

Second, CEP-DFT largely inherits the intrinsic challenges of modeling the EDL via implicit solvent and electrolytes. One limitation is the assumption that electrolyte ions relax adiabatically in response to structural changes. This may not be true, however, as the typical timescale of ion movement can range from picoseconds to nanoseconds, [504] whereas atomic motions occur within femtoseconds. CEP-DFT could therefore underestimate the free energies when the modeled processes are expected to occur within these timescales. On the other hand, reactive events are rare and occur on longer timescales. For example, the experimental Arrhenius plots show that the timescale for the hydrogen evolution reaction at the Pt electrode ranges between 5 to 200 picoseconds. [505] In such cases, our adiabatic treatment of ion relaxation is largely justified. Ref. [504] presents an in-depth discussion of the limitations of using LPB/PCM models for electrocatalysis.

Lastly, CEP-DFT alone cannot capture explicitly dynamical and entropic effects. The fluctuations present on the surface may make many different surface configurations energetically accessible. As the system complexity is increased, using a single structure to represent the catalyst state may be inappropriate to fully account for this dynamical nature of the electrode-electrolyte interface under operando conditions. For quantitative comparison to experimental data, CEP-DFT would therefore work best for systems that exhibit minimal dynamical character. For instance, the silver model presented in Chapter 3 was specifically compared to an experimental system that showed minimal nucleation and restructuring behavior. [447] To partially mitigate this approach, one may add entropic contributions under the harmonic approximation by computing vibrational/phonon modes of the slab. [11, 233] Nonetheless, molecular dynamics combined with importance sampling is desirable if enough computational resources are available.

Explicit Models for Electrochemical Reactions. If one needs to study factors that are best described by explicit atomic representations, CEP-DFT may not be adequate. Two such factors are pH and electrolyte effects, both of which are very important in electrochemistry. [411, 479, 506, 507] CEP-DFT can only account for these effects indirectly: electrolyte variations are modeled by adjusting the Debye length λ_D , and pH change is modeled by adjusting the reference voltage via the Nernstian relation between the Reversible and Standard Hydrogen Electrodes (RHE and SHE). Indeed, these treatments fail to capture explicit atomistic interactions. Below we provide a summary of two emerging approaches in the field that use explicit representations:

1. Ensemble representation of catalyst state [484, 508–511]: Instead of using a single or few selected structures, this approach represents a catalyst state as a statistical ensemble of different structures that correspond to the global minimum and the nearby local minima on the free energy surface. This model allows variation of the atomic composition in the unit cell for a designated element (e.g., hydrogen), which allows a rigorous representation

of constant pH conditions. The challenge of this approach is naturally the efficient search through chemical composition space, but recent developments in grand canonical genetic algorithm has made this approach more feasible. [17, 18, 20]

2. Constant-potential molecular dynamics (CPMD) [246, 247, 512–514]: These CPMD-based approaches are usually combined with constrained sampling [515, 516] to construct the potential of mean force. One recent development is the constant-potential hybrid-solvation dynamic model (CP-HS-DM), which sets the Fermi level of system to fluctuate around a desired value. [246, 247] CP-HS-DM is similar to CEP-DFT in that the number of electrons is allowed to vary, but it uses a more explicit representation of the solvent molecules in the EDL region.

The Future of Quantum Chemistry

The field of computational catalysis is currently undergoing a major change owing to the rapid development of machine-learning interatomic potentials (MLIPs). [67, 122, 517–519] Modern MLIPs trained on datasets containing ~ 100 million hybrid mGGA DFT calculations [120, 121] can now achieve performance that is comparable to the DFT methods used to obtain the training and validation data at a dramatically lower computational cost. As a result, this new generation of MLIPs is gaining significant traction within the catalysis and materials science communities.

While MLIPs will enable simulations with more atoms, quantum chemistry methods will still remain invaluable for uncovering quantum chemical insights that make catalysts work. In fact, the rapid integration of ML approaches may further propel quantum chemistry to go beyond ground state energies and towards more challenging physics and electronic structure. Here we provide an incomplete list of remaining challenges for quantum chemistry research:

1. Charge Transfer: Can mean-field DFT or quantum chemistry methods predict various types of interfacial charge transfer reactions properly? From the well-known challenge of CO binding on noble metals such as Pt to the dissolution of Cu adatoms to Cu^{2+} , almost everything that happens at the surface is governed by partial or complete charge transfer between subsystems. By definition, the exact exchange-correlation functional must describe them correctly. However, DFAs are known to incur charge delocalization errors and therefore it is very likely that widely used DFAs will fail to describe them properly. Future development of quantum chemical methods will also benefit from developing new formalisms to quantify/characterize the extent of charge transfer between subsystems and their changes. [520–522]
2. Methods for open system: Conventional quantum chemical tools are best suited for isolated systems. In contrast, the open external conditions applied to the electrified interface are central to realizing difficult reactions in heterogeneous catalysis. While there are recent efforts to treat these open, grand-canonical conditions as briefly mentioned in Chapter 1 (e.g., electrode potential [242, 243]), generalizing these frameworks beyond the special case of metal-solution interface to a broad range of conditions may yield new insights. [244, 245, 523]

3. Nuclear Quantum Effects (NQE): The importance of protons cannot be overstated in capturing the correct physics of the metal-solution interface. Key reaction pathways often involve consumption and generation of protons, which include electrolysis of H_2O or dissociative adsorption of H_2 . [228, 524, 525] As discussed in Chapter 1, the BO approximation treats the protons as point charges — but what if this approximation breaks down? In fact, numerous studies report that NQEs of protons are critical for accurately describing the structure of water and reactions within solution. [526–531] While there has already been great effort devoted to NQEs, [532–538] efficiently integrating such methods into quantum chemical tools and MLIPs will be beneficial for the accurate simulation of catalytic systems.
4. Correlated wavefunction theory: For some systems, we may have to step away from single-reference DFT in order to adequately treat strong/static electron correlation. For example, it is argued that high temperature superconductivity in cuprates is a demonstration of strong electron correlation, which is an effect that present-day DFAs cannot capture. [539–541] MLIPs trained on DFT energetics will likewise be unable to accurately describe strongly correlated systems as a consequence. Fortunately, recent advances in utilizing spatially localized atomic basis sets are increasingly becoming popular and are enabling weakly correlated wavefunction theory calculations on periodic systems. Integrating calculations beyond single-determinant density functional theory more routinely could also be helpful for these types of systems. [542–544] In turn, this will lay foundations for development of strongly correlated methods for periodic systems. Current methods in this front include theories based on dynamics or static embedding theory, [545–549] and more progress will allow routine simulations of strongly-correlated catalytic systems.

In conclusion, quantum chemistry will remain an integral part of the study of heterogeneous catalysis. Its role can be expanded beyond reaction energy estimates as more sophisticated physics are integrated into its underlying formalism. The catalysis community will benefit immensely from these new directions, particularly through models of charge transfer processes, inclusion of nuclear quantum effects, and robust wavefunction theories for strongly correlated electrons. There still exist numerous aspects of physics which conventional quantum chemistry has not yet fully explored, and the pursuit of these frontiers may define the next generation of quantum chemistry and its role in heterogeneous catalysis.

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Appendix A

Additional Details on the CEP Protocol

A.1 Fractional Electrons in KS-DFT

Many of the quantum chemistry methods consider systems with integer number of electrons, which cannot fully describe inherently grand-canonical, open-systems because fractional electrons represent an averaged behavior. In fact, fractional number formalism and its application in Kohn-Sham Density Functional Theory (KS-DFT) has been actively studied since the birth of its theory. [339, 550] To briefly introduce, fractional number can be introduced in occupation number n_i used in electron density

$$\rho(r) = \sum_i n_i |\psi_i(\vec{r})|^2. \quad (\text{A.1})$$

where $n_i \in [0, 1]$. This allows one to find possible solutions for the corresponding electron density ρ , even for non-integer number values of n_i . Perdew and co-workers showed that the electronic energy of such non-integer number of electrons is exactly determined via a linear interpolation between the nearest two integer electrons energies,

$$E(N - x) = E(N) + x[E(N - 1) - E(N)], \quad (\text{A.2})$$

where $x \in [0, 1]$ and N is an integer. [339] A conceptually simple understanding of this piecewise-linearity can be obtained from Yang *et al.* [551] In this work, a fractional number electron is explained using a statistical mixture comprised of non-interacting, identical copies. Since the mixing of degenerate, non-interacting do not affect the total energy, the electronic energy of this mixture is thus aligned with the form of Eqn. (A.2). Study of fractional number problem extends to be very important in the design of approximate KS-DFT, [106] and we recommend interested reader to the appropriate references.

A.2 Constant Electrode Potential (CEP) Model

Constant Electrode Potential (CEP) model [235, 504] makes use of the fractional number formalism described in the previous section. The desired electrode potential with respect to the Standard

Hydrogen Electrode (SHE) ϕ_{SHE} can be calculated with the Fermi level ε_F using

$$\Phi = \frac{-\varepsilon_F - \phi_{\text{SHE}}}{e}. \quad (\text{A.3})$$

In a CEP calculation, the number of electrons is fractionally varied in order to align the Fermi level of the bulk metal with the applied potential bias such that it meets Eqn. (A.3) to a desired convergence criteria value of $d\Phi$. In practice, this procedure is implemented through adding an extra step of self-consistent loop, on top of the usual electronic minimization of the Kohn-Sham orbitals followed by the structural relaxation of the molecules. Because the CEP model works via varying the number of electrons, the energy of interest of the model is consequently not the electronic energy of the cell on its own, but the free energy (relevant to the grand potential):

$$G(\Phi) = E(\Phi) - q\Phi \quad (\text{A.4})$$

where E is the electronic energy, q the total charge of the system, and Φ the applied potential calculated via Eqn. (A.3). Correction to the finite cell height can also be incorporated in the electronic energy as well [433] which has been reported to important for more accurate energetics. [417] In this work, we have taken this additional correction into account. CEP model is therefore a particular type of Grand-Canonical DFT (GC-DFT). [242, 552] We note that CEP model is often employed with implicit solvent model that can provide countercharges to ensure a net neutral unit cell, with the most popular choice being the Polarizable Continuum Model/Linearized Poisson-Boltzmann (PCM/LPB) implicit solvation.

Appendix B

Additional Information for Extending Orbital-Optimized Density Functional Theory to L-edge XPS and Beyond

B.1 The 1eX2C- Z_{eff} Hamiltonian

The empirical scaling relationship utilized by the 1eX2C- Z_{eff} Hamiltonian is described in Refs [319–321]. These relationships were determined via forming an effective one-electron Breit-Pauli Hamiltonian with an empirical nuclear charge Z_{eff} as a fitting parameter:

$$\hat{h}_1^{\text{Breit-Pauli}} \simeq \frac{\alpha^2}{2} \sum_{i,A} \frac{Z_{\text{eff},A}(Z)}{r_{iA}^3} \hat{L}_{iA} \cdot \hat{S}_i \quad (\text{B.1})$$

where α is the fine structure constant, index i runs over electrons, index A runs over nuclei, $\hat{L}$ represents the orbital angular momentum operator, and $\hat{S}$ represents the spin angular momentum operator. The effective nuclear charges were determined via low-lying excited states of small molecules and their corresponding fine structure splittings. Specifically, MCSCF calculations with empirical $Z_{\text{eff},A}$ were performed to replicate experimental values for low-lying triplet/doublet states, in combination with a non-relativistic Hamiltonian.

To compute the corresponding one-body X2C operator $\hat{h}_1^{\text{X2C-}Z_{\text{eff}}}$ from the empirical effective nuclear charges, we first compute $\hat{W}_{\text{SO}}^{Z_{\text{eff}}}$ via

$$\hat{W}_{\text{SO}}^{Z_{\text{eff}}} \equiv \hat{\vec{p}} \times \hat{V}^{Z_{\text{eff}}} \hat{\vec{p}} \quad (\text{B.2})$$

$$\hat{V}^{Z_{\text{eff}}} \equiv \sum_{i,A} \frac{Z_{\text{eff},A}}{r_{iA}} \quad (\text{B.3})$$

where effective nuclear charge is included in the nuclear attraction operator. This $\hat{W}_{\text{SO}}^{Z_{\text{eff}}}$ and $\hat{W}_{\text{SF}}$ are used to compute $\hat{W}^{Z_{\text{eff}}} = \hat{W}_{\text{SF}} + i\hat{\vec{\sigma}} \cdot \hat{W}_{\text{SO}}^{Z_{\text{eff}}}$. Note that the effective nuclear charges do not enter the

spin-free part of $\hat{W}^{Z_{\text{eff}}}$. This is motivated by the observation that most treatment of effective SOC under 1eX2C formalism attempts to parametrize the spin-dependent part only. Once the matrix $\mathbf{W}^{Z_{\text{eff}}}$ is computed, we solve the four-component one-body Dirac equation via:

$$\begin{bmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & \frac{\mathbf{W}^{Z_{\text{eff}}}}{4c^2} - \mathbf{T} \end{bmatrix} \begin{bmatrix} \mathbf{C}_L \\ \mathbf{C}_S \end{bmatrix} = \epsilon \begin{bmatrix} \mathbf{S} & 0 \\ 0 & \frac{1}{2c^2} \mathbf{T} \end{bmatrix} \begin{bmatrix} \mathbf{C}_L \\ \mathbf{C}_S \end{bmatrix} \quad (\text{B.4})$$

This yields the corresponding decoupling and renormalization matrices $\mathbf{X}^{Z_{\text{eff}}}$ and $\mathbf{R}^{Z_{\text{eff}}}$. These matrices can be used to obtain the desired one-body model X2C operator with effective nuclear charges, $\hat{h}_1^{\text{X2C-Z}_{\text{eff}}} = \hat{T}^{\text{X2C-Z}_{\text{eff}}} + \hat{V}^{\text{X2C-Z}_{\text{eff}}}$, using:

$$\mathbf{T}^{\text{X2C-Z}_{\text{eff}}} = \left(\mathbf{R}^{Z_{\text{eff}}} \right)^\dagger \left[\mathbf{X}^{Z_{\text{eff}}} + \left(\mathbf{X}^{Z_{\text{eff}}} \right)^\dagger \mathbf{T} - \left(\mathbf{X}^{Z_{\text{eff}}} \right)^\dagger \mathbf{T} \mathbf{X}^{Z_{\text{eff}}} \right] \mathbf{R}^{Z_{\text{eff}}} \quad (\text{B.5})$$

$$\mathbf{V}^{\text{X2C-Z}_{\text{eff}}} = \left(\mathbf{R}^{Z_{\text{eff}}} \right)^\dagger \left[\mathbf{V} + \frac{1}{4c^2} \left(\mathbf{X}^{Z_{\text{eff}}} \right)^\dagger \mathbf{W}^{Z_{\text{eff}}} \mathbf{X}^{Z_{\text{eff}}} \right] \mathbf{R}^{Z_{\text{eff}}}. \quad (\text{B.6})$$

The resulting one-electron operator is then combined with non-relativistic two-electron operator as described in main text.

B.2 Computational Aspects of NO-QDPT

B.2.1 Treatment of the core-hole ROHF MO coefficients

To properly treat SOC effects within NOCI using $\hat{H}^{\text{1eX2C-model}}$, the core-ionized states $\{|\Psi_n\rangle\}$ must be prepared in matrix form suitable for complex Generalized Hartree Fock (cGHF) calculations. For NO-QDPT, however, the SOC effects are only introduced while diagonalizing $\hat{H}^{\text{1eX2C-model}}$ but not while optimizing the core-ion states, which are obtained through restricted open-shell HF/DFT calculations. Therefore, the coefficient matrix $\mathbf{C}$ for cGHF molecular orbitals is a $\mathbb{C}^2$ matrix of dimensions $2N_{AO} \times 2N_{AO}$, whereas the core-ion MO coefficients $|\Psi_N\rangle$ are obtained as $\mathbb{R}^2$ matrices of dimensions $N_{AO} \times N_{AO}$ (N_{AO} : number of AO basis). This requires a proper transformation of the ROHF MO coefficient matrix ($\mathbf{C}_n \in \mathbb{R}^2$) for it to be compatible with the computation of matrix elements of the 1eX2C-model Hamiltonian matrix ($\mathbf{H}^{\text{1eX2C-model}}$), which is specified below.

1. Obtain n states with localized holes $\{|\Psi_n\rangle\}$, using ROHF (or RO-DFT) calculations with spin-free 1eX2C Hamiltonian $\hat{H}^{\text{SF-1eX2C}}$. The occupied block of the MO coefficients $\mathbf{C}_{\text{occ},n}$ will have dimensions of $N_{AO} \times (N_{\text{occ}} - 1)$, where N_{occ} is the number of occupied spatial MOs for the ground state RHF calculation (and thus half the number of electrons in ground state).
2. Define hole-reattached determinants $|\Psi^n\rangle = \hat{a}_n^\dagger |\Psi_n\rangle$ and its corresponding occupied MO coefficient matrix as $\mathbf{C}_{\text{occ}}^n$. This is simply done by adding an extra column corresponding to the localized hole on C_n and is therefore a $N_{AO} \times N_{\text{occ}}$ matrix.

3. In a cGHF calculation, determinants with α and β holes must be represented with different columns of MO coefficient matrices. We obtain the real parts of each MO coefficient for NO-QDPT using direct sum:

$$\mathbf{C}_{2n-1} = \mathbf{C}_{\text{occ},n} \oplus \mathbf{C}_{\text{occ}}^n \quad (\text{B.7})$$

$$\mathbf{C}_{2n} = \mathbf{C}_{\text{occ}}^n \oplus \mathbf{C}_{\text{occ},n}. \quad (\text{B.8})$$

Both $\mathbf{C}_{2n-1}$ and $\mathbf{C}_{2n}$ have dimensions of $2N_{AO} \times 2N_{\text{occ}} - 1$. Note that $\mathbf{C}_{2n-1}$ and $\mathbf{C}_{2n}$ are permutations of each other. For the imaginary part, simply use a zero matrix of dimensions $2N_{AO} \times (2N_{\text{occ}} - 1)$. Use $\mathbf{C}_{2n-1}$ and $\mathbf{C}_{2n}$ in combination with the zero matrix to obtain complex-valued matrices $\tilde{\mathbf{C}}_{2n-1}, \tilde{\mathbf{C}}_{2n} \in \mathbb{C}^2$ with dimensions $2N_{AO} \times 2N_{\text{occ}} - 1$.

4. Our states are now suitable for computing NOCI matrix elements[187] $\mathbf{H}_{AB}^{\text{leX2C-model}}$ and $\mathbf{S}_{AB}$ using the complex-valued matrices $\tilde{\mathbf{C}}_A$ and $\tilde{\mathbf{C}}_B$ for the determinants A and B .

B.2.2 Preparation of the ground state

To obtain excitation or ionization energy, one can either subtract these energies from the true cGHF ground-state (GS) solution or the RHF ground-state solution with a perturbative correction of SOC at the ground-state. In this work, we chose the latter as it permits the use of Kohn-Sham determinants without implementing a non-collinear form of the DFT kernels. Same treatment as previous section can be done for compatibility with cGHF calculation but in a much simpler form, which would involve a matrix tensor product between the 2×2 identity matrix and the ground state RHF MO coefficient matrix.

B.2.3 Preparation of the localized hole determinants

For NO-QDPT, each core-hole must be localized and the resulting determinants be orthogonal (or near-orthogonal) to each other. We found the following strategies to be useful in achieving these conditions:

1. Feeding in a ground state guess obtained with a small electric field. This has an effect of breaking the (near-) degeneracy of inner-shell orbitals and orienting them in specific directions. This enables us to obtain the states of interest under the spin-free Hamiltonian without mixing of inner-shell orbitals with different L_z values.
2. For systems with multiple ionization/excitation centers (*e.g.*, Cl_2): Performing a Boys Localization on a converged ground state calculation (after SCF) and then feeding in this guess. Alternatively, applying a small electric field can also break the spatial symmetry of the orbitals as well.
3. For Kohn-Sham determinants: Computing exchange-correlation contributions with finer grids, to minimize errors arising from the lack of rotational invariance.

To examine the orthogonality of the Slater determinants within the NOCI subspace, we performed singular value decomposition (SVD) on the NOCI overlap matrices ($\mathbf{S}$) for the 3rd row species noted in Fig. 2 of main text and found that all the singular values are within $[0.99, 1.01]$. This indicates that there are virtually no linear dependencies within the NOCI subspace. However, as this check must be done *a posteriori* after optimization of all core-hole states, a constrained optimization scheme where strict orthogonality between all core-hole states involved in a NOCI calculation are imposed throughout the Δ SCF iterations would be helpful and desirable.

B.3 Computational Details for Δ cGHF calculation

To compute the L_2 and L_3 ionization energies via state-specific Δ SCF calculations in complex-generalized Hartree Fock (Δ cGHF), six 2p-like spin-orbitals of a ground state calculation were ionized and optimized. Since Δ cGHF calculations were performed for Ar, HCl, H_2S , PH_3 , and SiH_4 , the ionization targets were the 5th to 10th lowest energy orbitals. The ionized states were optimized via the Maximum Overlap Method.[169]

The optimized Δ cGHF calculations led to six different states, with four states of near-identical energies corresponding to L_3 ionization and two higher energy states of near-identical energies corresponding to L_2 ionization. We note that the lack of perfect fourfold degeneracy within the L_3 band and perfect twofold degeneracy within the L_2 band arises from spherical symmetry breaking due to molecular field (and hence does not occur for Ar). The band average ionization energies were reported as Δ cGHF L_2 and L_3 CEBEs. Finally, the difference of L_2 IP and L_3 IP was reported as the Δ cGHF DS value.

B.4 Alkali Atom D-lines Splitting

We have also extended our approach to calculating D1-D2 splitting of alkali atoms. This excitation corresponds to the valence $ns^1 \rightarrow np^1$ excitation, where a splitting between two different D lines can be observed due to SOC. Table B.1 shows the % errors in gas phase D-line splittings computed through NO-QDPT, vs experiment. We note that while percentage error reported for D-line splitting themselves look sub-optimal, this is largely due to the small scale of the experimental energies we are computing the % error against (as small as 0.34 cm^{-1} for Li, while typical thermal fluctuation $k_B T \sim 200 \text{ cm}^{-1}$ for 300 K). SCAN0 reports merely a $\sim 15\%$ or lower error with DCB-SNSO, a remarkable performance considering the very small magnitude of the energy scale we are investigating.

B.5 Full Results for $L_{2,3}$ Edges for 3rd Row Element

Table B.2 lists the molecules containing 3rd row elements selected to evaluate the performance of NO-QDPT for the 3rd row elements in this work. Experimental results for $L_{2,3}$ edge IPs as well as its double splitting are given.

		Li	Na	K	Rb	Cs
Expt. (cm⁻¹)		0.34	17.20	57.71	237.60	554.04
		[553]	[554]	[555]	[556, 557]	[558, 559]
Method	Model ($\hat{H}$)	Error (%)				
HF	X2C	357.0	-4.7	-27.7	-36.5	-42.3
SCAN	X2C	217.0	42.9	11.4	1.0	-6.4
SCANh	X2C	166.9	39.3	9.1	-0.7	-7.9
SCAN0	X2C	106.9	34.1	6.0	-3.4	-10.4
B3LYP	X2C	712.5	63.2	28.9	15.3	4.5
ω B97X-D3	X2C	631.3	67.2	-8.1	-18.7	-26.0
ω B97X-V	X2C	462.1	40.9	5.3	-7.3	-17.1
BHLYP	X2C	1038.2	41.9	10.9	-1.5	-10.7
HF	DCB-SNSO	-95.5	-30.4	-39.0	-41.6	-45.4
SCAN	DCB-SNSO	161.5	4.4	-6.0	-7.1	-11.5
SCANh	DCB-SNSO	91.6	1.7	-7.9	-8.7	-12.8
SCAN0	DCB-SNSO	4.5	-2.1	-10.5	-11.2	-15.2
B3LYP	DCB-SNSO	466.6	19.2	8.8	6.0	-1.2
ω B97X-D3	DCB-SNSO	444.8	45.3	-22.5	-25.2	-30.0
ω B97X-V	DCB-SNSO	-33.4	2.9	-11.2	-14.7	-21.6
BHLYP	DCB-SNSO	905.4	3.6	-6.4	-9.4	-15.5

Table B.1: Gas phase alkali D-line splittings calculated through NO-QDPT. Orbitals were computed using the decontracted aug-cc-p ω CVTZ-X2C[372] (K, Rb, Cs) basis set and decontracted aug-cc-pVTZ[161] (Li, Na) basis set. The predicted values and the experiment are in wavenumbers (cm⁻¹) and the errors are reported in percent (%). Full results are available in our separately provided spreadsheet.

B.6 Performance of Z_{eff} Hamiltonian with NO-QDPT for elements beyond 3rd Row

We briefly describe the performance of Z_{eff} beyond third row elements in predicting the $L_{2,3}$ edge DS. The estimate of $L_{2,3}$ edge DS with Z_{eff} Hamiltonian is provided in Table B.3. Compared against the DCB-SNSO Hamiltonian, the performance of Z_{eff} Hamiltonian is notably degraded as the nuclear charge is increased. Especially, the doublet splitting values for the transition metals are

18-electron Series	Expt. L ₂ IP (eV)	Expt. L ₃ IP (eV)	Expt. DS (eV)	Ref.
Ar	250.78	248.63	2.15	[356]
HCl	209.03	207.40	1.63	[357]
H ₂ S	171.56	170.36	1.20	[358]
PH ₃	137.95	137.05	0.90	[359]
SiH ₄	107.80	107.20	0.60	[360]
Others	Expt. L ₂ IP (eV)	Expt. L ₃ IP (eV)	Expt. DS (eV)	Ref.
CH ₃ Cl	207.90	206.26	1.64	[363]
ClF	210.83	209.18	1.65	[363]
ClF ₃	214.62	213.02	1.60	[560]
Cl ₂	209.45	207.82	1.63	[363]
CCl ₄	208.73	207.04	1.69	[363]
SO ₂	176.00	174.80	1.20	[561]
CSO	171.80	170.60	1.20	[562]
CS ₂	171.00	169.80	1.20	[562]
SF ₆	181.48	180.27	1.21	[563]
SPF ₃ ^a	171.06	169.86	1.20	[564]
PF ₃	141.97	141.04	0.93	[565]
P(CH ₃) ₃	136.85	135.95	0.90	[359]
P(CF ₃) ₃	139.35	138.45	0.90	[359]
PCl ₃	140.50	139.60	0.90	[565]
PF ₅	145.14	144.31	0.83	[566]
OPF ₃	143.86	142.96	0.90	[564]
Si(CH ₃) ₄	106.55	105.94	0.61	[567]
SiCl ₄	110.76	110.17	0.59	[567]
SiF ₄	112.20	111.60	0.60	[568]
Si(OCH ₃) ₄	108.03	107.42	0.61	[569]

Table B.2: Experimental gas phase L-edge values for 3rd row element containing molecules tested in this work. ^aThe experimental value given for SPF₃ corresponds to ionization of sulfur.

erratic, reaching error of > 3 eV for DS for Kr. Similar error trends are also observed in the absolute L₃ edge values, though with a reduced magnitude. While the results show that early main group

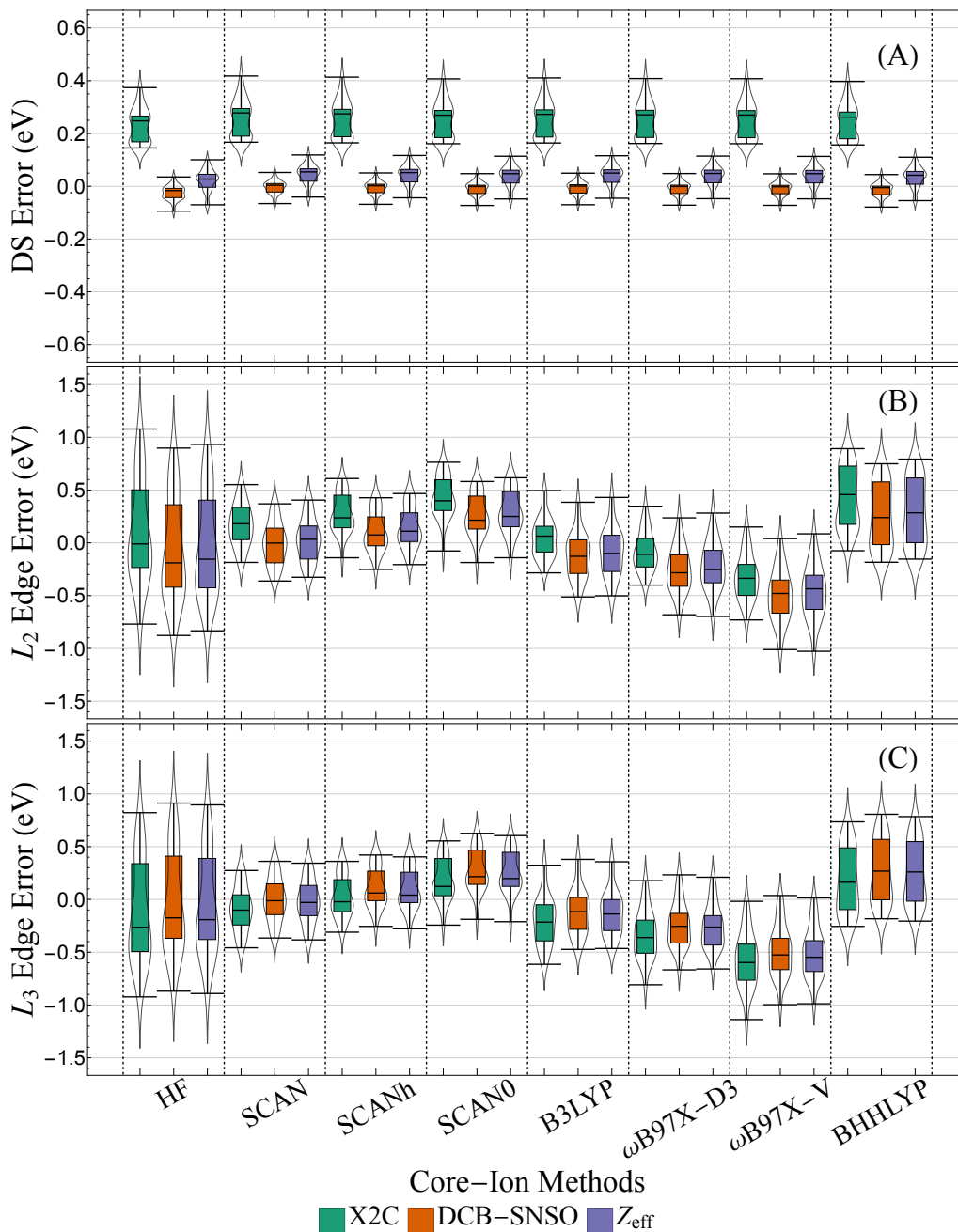


Figure B.1: Full violin plot results for the gas phase 3rd row element $L_{2,3}$ -edges. Boxes span the 50% as the interquartile range with the median noted, and the underlying contours show the distribution of the data.

parametrization of the effective nuclear charges[320] is relatively better than the transition metal parametrization[321], the lack of consistent performance as well as its worse performance when

Expt. L_3 (eV)		Z_{eff} Error (eV)	DCB-SNSO Error (eV)
Ca [368]	357.6	-0.6	-0.4
Cr(CO) ₆ [378]	582.0	0.3	0.7
Fe(CO) ₅ [570]	715.8	-0.3	0.2
Zn [369]	1029.1	-0.6	0.2
GeH ₄ [370]	1225.7	-0.3	0.7
Kr [371]	1679.2	0.3	1.8
Expt. DS (eV)		Z_{eff} Error (eV)	DCB-SNSO Error (eV)
Ca [368]	3.4	0.7	0.1
Cr(CO) ₆ [378]	8.8	0.6	-0.6
Fe(CO) ₅ [379] ^a	12.3	1.0	-0.7
Zn [369]	23.2	2.1	-0.4
GeH ₄ [370]	31.1	2.4	-0.7
Kr [371]	52.7	3.2	-1.4

Table B.3: L_3 edge and $L_{2,3}$ DS values for elements beyond 3rd row using NO-QDPT and HF core-ions. The performance based on Z_{eff} Hamiltonian is compared against that of DCB Hamiltonian.
^aThe experimental value of DS given for Fe(CO)₅ corresponds to the DS of the lowest dipole-allowed transition. Same basis sets were used for each molecular species as shown in main text.

compared to DCB-SNSO parametrization indicates that effective nuclear charge based approach is less robust.

The poor performance of the Z_{eff} might mostly arise from shortcomings in its parametrization, which is based on valence properties of diatomic hydrides for main-group elements calculated with MCSCF/SBK(d,p).[319, 320] Z_{eff} approach is therefore agnostic to orbital angular momentum, screening the full SOC operator by the same scaling factor. In contrast, SNSO-based approaches compare orbital energies between four-component and two-component calculations in order to propose a shell-dependent scaling factor. A better parametrization of Z_{eff} factors with more sophisticated SOC Hamiltonian with quantities more relevant to core-level splitting may lead to a better performance. As such, we only report results from the SNSO-based parametrization schemes on the main text.

B.7 Delocalization Errors for Kr Inner-Shell Ionization

Orbital	a	b	r^2	Non-relativistic binding energy (eV)
1s	0.012	0.989	0.9967	14095.9
2s	0.016	0.984	0.9999	1851.4
2p	0.020	0.980	0.9999	1678.5
3s	0.043	0.957	1.0000	272.6
3d	0.111	0.889	0.9999	95.4
4s	0.186	0.813	0.9999	28.4
4p	0.312	0.688	1.0000	14.1

Table B.4: Deviations from linearity[339] for fractional ionization of Kr orbitals with nonrelativistic, spin-unrestricted SCAN calculations. Following Ref. [106], the SCAN energies $E(x)$ upon removal of x fractional alpha electrons from the specified orbital are approximated with $E(0) + x(ax + b)(E(1) - E(0))$ (where $E(0)$ is the energy of the neutral atom, and $E(1)$ the energy after the complete removal of an electron). The corresponding a, b are found from linear fits of $\frac{1}{x} \frac{E(x) - E(0)}{E(1) - E(0)}$ vs x , and are reported below along with the corresponding r^2 values for the linear fits. The inner-shell orbitals have the smallest curvatures a , indicating lower deviation from piecewise linearity. The $3p$ ionization led to several convergence failures, and is thus not reported.

Appendix C

Additional Information for Understanding Ion-transfer Reactions in Silver Electrodeposition and Electrodeposition

C.1 Design of the Solvation Model

C.1.1 Fully Implicit Solvation Model

The free energy profile of the fully implicit solvent and electrolyte representation is shown below in Figure C.1. First, fully implicit description of the electrolyte and solvent successfully captures the generation of Ag^+ but fails to capture the correct thermodynamics of the reaction. On the right panels of Figure C.1, the partial charge changes using the iterative Hirshfeld partitioning scheme correctly captures the localized +1 charge in the departing Ag atom for all electrode potentials, while mostly maintaining the bulk charge unchanged. However, corrosion is described thermodynamically unfavorable, even for the highest electrode potential of 1.00 V vs. SHE. Given that the standard reduction potential of Ag is 0.80 V vs. SHE, [443] a potential of +1.00 V is expected to describe the corrosion of an adatom as thermodynamically favored, but the fully implicit description of solution shown by Figure C.1 fails to capture this important property. This highlights that the implicit solvation model provides insufficient solvation for ionic species, necessitating further correction to our solvation model.

C.1.2 The Hybrid Solvation Model: Choice of Two Explicit Waters

In order to obtain a more accurate energy profile, we investigated the most efficient but physical hybrid solvation model required to obtain the correct energetics. We observed that providing sufficient stabilization to the Ag^+ at the dissociated limit would correct the free energies of Figure C.1. To this end, we optimized various Ag cation structures with explicit water solvation shell geometries, in the presence of implicit polarizable continuum model (PCM) solvation, to identify any saturation behavior in the hydration energy. Specifically, the formation of Ag^+ solvation shell with n water

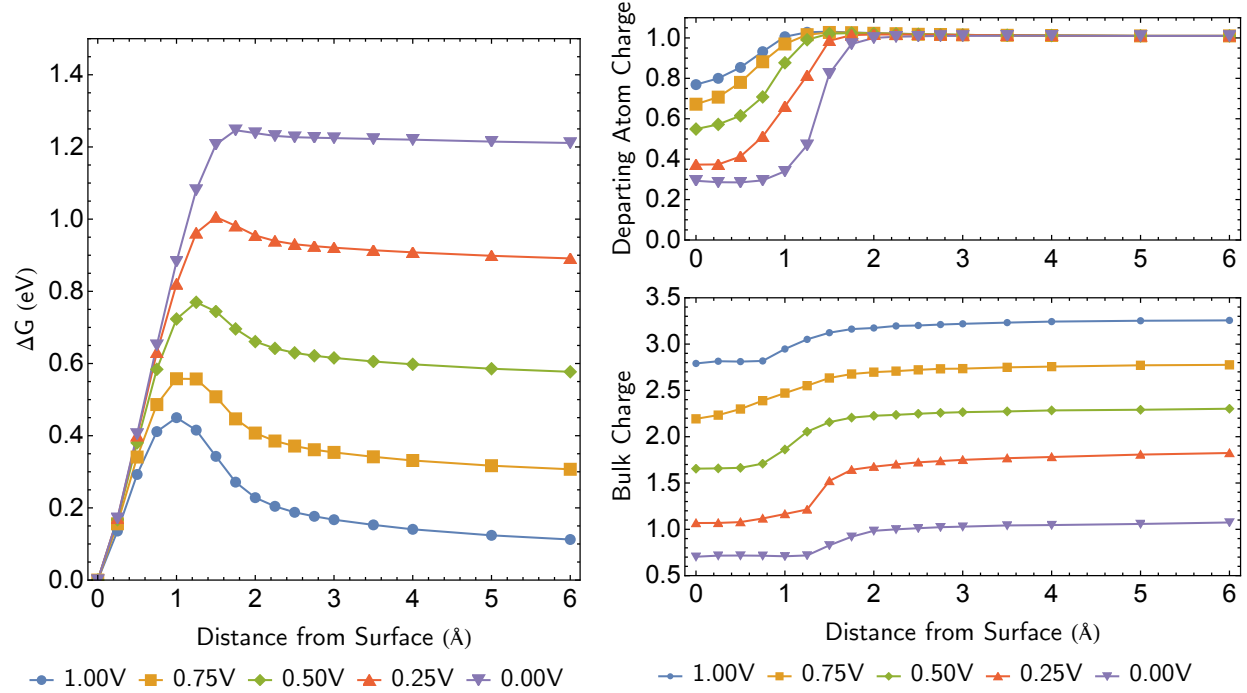
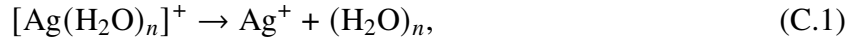


Figure C.1: Last-atom-bound corrosion with fully implicit description of the solvent/electrolyte in Ag_{25} . (left) The change in the free energy with respect to the vertical drift of the departing Ag. (right) The change of partial charges for the departing Ag and the bulk. The bulk charge is the sum of the partial charges of the 24 Ag atoms in the lattice.

molecules is described by the reaction



and therefore the energy gain by using n explicit water molecules on top of an implicit solvation is

$$\Delta E_{\text{hydration}}^{\text{PCM}} = \left(E_{(\text{H}_2\text{O})_n}^{\text{PCM}} + E_{\text{Ag}^+}^{\text{PCM}} \right) - E_{[\text{Ag}(\text{H}_2\text{O})_n]^+}^{\text{PCM}}. \quad (\text{C.2})$$

The results of this calculation are shown in Table C.1. Noticeably, there is only a minimal variation in the explicit hydration energies after two explicit water molecules, $n = 2$. This means that two explicit waters in the planar geometry ($[\text{Ag}(\text{H}_2\text{O})_2]^+$) are sufficient to provide enough stabilization. The total solvation energies, which are calculated by adding the energy difference between Ag^+ in vacuum and Ag^+ in PCM-only (3.481 eV) onto the values of $\Delta E_{\text{hydration}}^{\text{PCM}}$, shows the total solvation energies are qualitatively aligned with the experimentally observed value of 5 eV. We therefore chose to add two explicit water molecules around the departing Ag^+ cation and used it for CEP calculations. We note that this procedure is can be easily generalized to different solvent systems.

Number of explicit waters (n)	0	1	2	3	4	5	6	8
$\Delta E_{\text{hydration}}^{\text{PCM}}$ (eV)		0.583	1.114	1.262	1.172	1.133	1.309	1.066
Total Solvation Energy (eV)	3.481	4.063	4.594	4.743	4.653	4.614	4.789	4.546

Table C.1: Explicit hydration energy $\Delta E_{\text{hydration}}^{\text{PCM}}$ and the total solvation energy for Ag^+ solvation shell with n explicit waters. The total solvation energies for the case of $n \neq 0$ waters are calculated by adding the energy gain using PCM-only (*i.e.*, 3.481 eV) and the corresponding explicit hydration energy $\Delta E_{\text{hydration}}^{\text{PCM}}$.

C.2 Supplementary Data for Adatom Anodic Dissolution/Deposition

C.2.1 Bulk Redox Potential of Ag

The bulk standard reduction potential of Ag was calculated through the following thermochemical cycle:

1. Sublimation Energy: $\text{Ag(s)} \longrightarrow \text{Ag(g)}$
2. Ionization Energy: $\text{Ag(g)} \longrightarrow \text{Ag}^+(\text{g}) + \text{e}^-$
3. Solvation Energy: $\text{Ag}^+ + 2 \text{H}_2\text{O} \longrightarrow [\text{Ag}(\text{H}_2\text{O})_2]^+(\text{aq})$ (+VASPsol)

The sublimation energy of Ag was calculated by constructing a 2x2x2 supercell (5 layers of 8 atoms) of Ag(100) (with the same dimension of the box used in the CEP calculations of this work), and consequently calculating the energy change associated with removing the Ag atom at the center of the third layer and placing it between the two periodic images. The ionization energy of Ag was calculated on a $20 \text{ \AA} \times 20 \text{ \AA} \times 20 \text{ \AA}$ box with Ag and Ag^+ placed on the center. The calculation of Ag^+ incorporated dipole correction on all directions. For the solvation energy, the optimized 2 H_2O structure, determined in the previous section (while designing the solvation model), was placed in the same $20 \text{ \AA} \times 20 \text{ \AA} \times 20 \text{ \AA}$ cubic box. This energy was summed with the energy of the Ag cation and compared against the energy of $[\text{Ag}(\text{H}_2\text{O})_2]^+$ embedded in VASPsol. The calculated energy for each component is tabulated in Table C.2. All of the calculations employed VASP for consistency with the RPBE functional. Ionization energy and sublimation energy was calculated with Gamma-point only Monkhorst-Pack grid, while the sublimation energy was calculated with $6 \times 6 \times 1$ Monkhorst-Pack grid. Summing each of the components and subtracting by 4.43 eV (the theoretical work function of SHE) results in 0.82 V vs. SHE, which is in very good agreement with the experimentally reported Ag bulk redox potential.

Sublimation Energy			
	2x2x2 supercell	2x2x2 supercell with center Ag displaced	ΔE
Energy (eV)	-82.610643 eV	-79.704438 eV	2.91 eV
Ionization Energy			
	Ag(g)	Ag ⁺ (g)	ΔE
Energy (eV)	-0.020988 eV	7.630450 eV	7.65 eV
Solvation Energy			
	Ag ⁺ + 2 H ₂ O	[Ag(H ₂ O) ₂] ⁺ (aq) (+VASPsol)	ΔE
Energy (eV)	-20.785855 eV	-26.095840 eV	-5.31 eV

Table C.2: Components used in the calculation of bulk Ag standard reduction potential.

C.2.2 Interfacial Capacitance

To estimate the effect of two explicit waters on the interfacial capacitance, we used the 1.00 V optimized structure of Ag₂₅ at 0.00 Å displacement above surface normal (including the two explicit waters) and varied the charge in the cell to observe the linear response of the voltage and subsequently calculate capacitance via $C = dq/dV$. Although this is a rough approximation, this provides a good ballpark approximation to gauge the effect of two explicit waters. The calculated values as well as the linear fitted slope are tabulated in Table C.3. The resulting value of the slope is estimated to be 2.033×10^{-19} C/V, and divided by the area of xy -plane of our cell (70.8079 Å², both sides of the slab gets charged) results in interfacial capacitance of 0.1436 F/m², which is lower than the value of 0.4 F/m² experimentally observed, [571] but qualitatively correct by being in the right order of magnitude.

$N_{\text{electrons}}$ (eV)	290.5	290	289.5	289	291.5	292	292.5	293
Charge on cell (e_0)	+0.5	+1.0	+1.5	+2.0	-0.5	-1.0	-1.5	-2.0
Voltage (vs. SHE)	-0.808	-0.457	-0.178	0.107	-1.648	-2.070	-2.560	-2.964
Slope: 2.033×10^{-19} C/V								
Fit Results: $R^2 = 0.9939$								

Table C.3: Calculation of interfacial capacitance.

C.3 Supplementary Data for Corrosion from the perfectly-flat surface (Ag_{24})

This section lists supplemental data relevant to simulating defects in corrosion/deposition which are the perfectly-flat (Ag_{24}) case.

C.3.1 Pathway Dependence of the Partial Charges for Ag_{24}

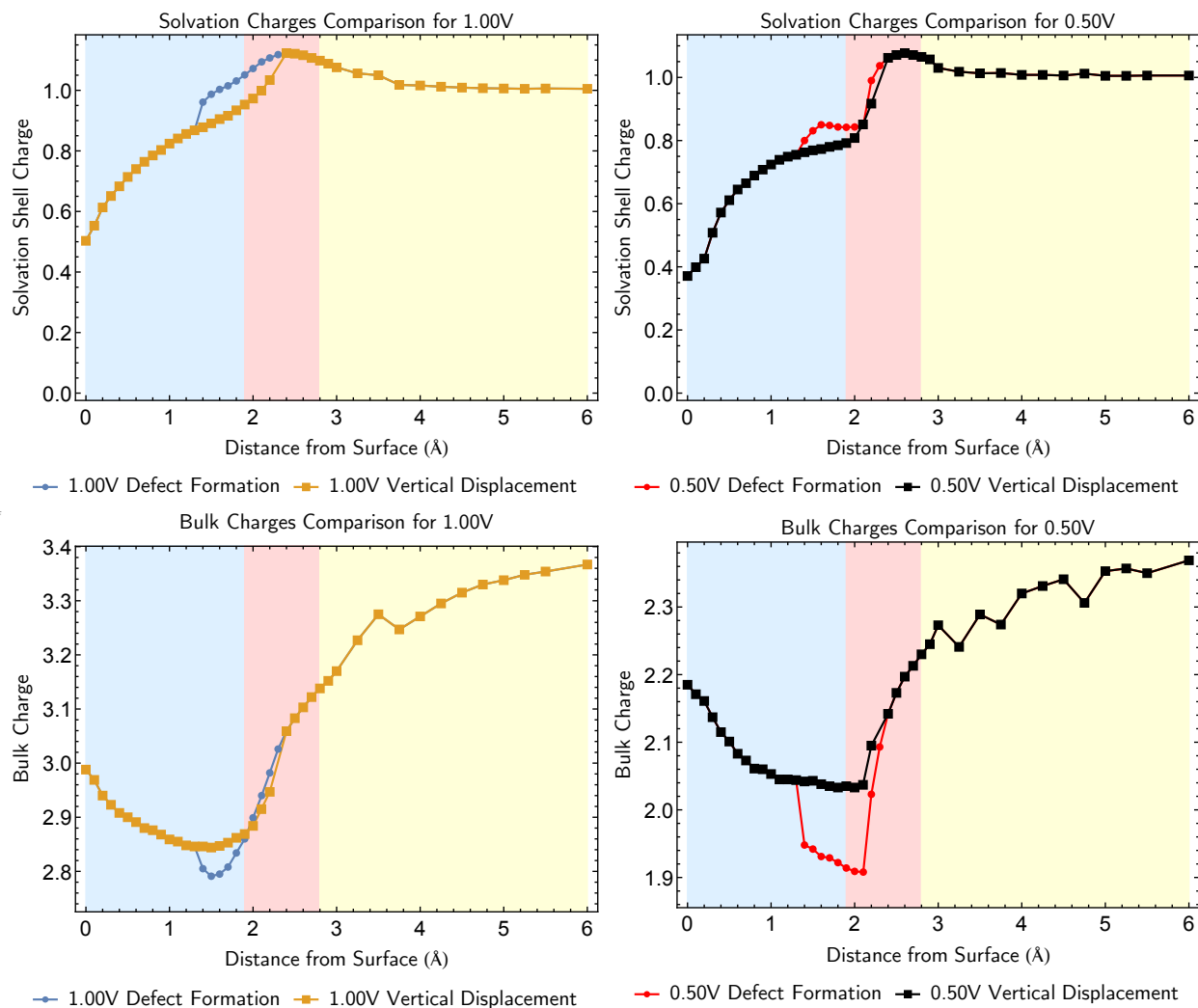


Figure C.2: Potential Dependence of the horizontal drift in defect-formation pathway.

Figure C.2 shows that the defect-formation pathway induces more changes in the partial charges in the detachment step (pink region) in the course of corrosion/deposition, both in the solvation

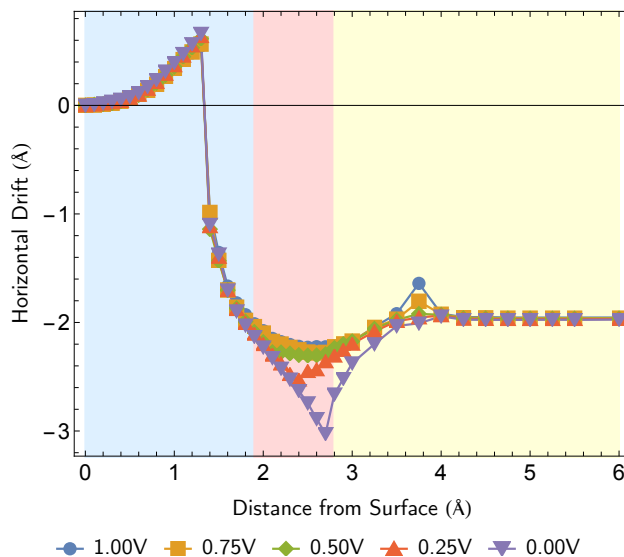


Figure C.3: Potential dependence of the departing solvation shell’s horizontal for Ag_{24} defect-formation pathway. Since the horizontal drift is confined to one-dimension, the value can be plotted as a signed to quantity to indicate the direction of the drift. In this plot, a 0 Å horizontal drift represents a vertical displacement above the vacancy position.

shell and in the bulk. This is explained by the horizontal drift associated with the defect-formation pathway, which causes the departing atom to be placed closer to the $\text{Ag}(100)$ surface than the vertical pathway. This induces stronger “image”-type charge interactions between the solvation shell and the bulk.

C.3.2 Potential Dependence of the Drift in Ag_{24} Corrosion

Figure C.3 shows that lower potentials result in more horizontal drift fluctuations in the defect-formation pathway of Ag_{24} . This is most evident in the detachment step (pink region) of the Ag_{24} . This can be explained by the stronger metal-metal interaction under the presence of lower potential condition, when compared stronger anodic conditions.

C.3.3 Thermodynamics of the Ag_{24} Case

In Table C.4, the absolute free energies for uncorroded/corroded structures under strong potentials of 1.25 V and 1.50 V are provided for Ag_{24} . The results show that application of very strong potentials eventually leads a favorable corrosion, assuring the qualitative correctness of the CEP calculations on this model.

Potential (V)	G of Ag_{24} 0 Å structure (eV)	G of Ag_{24} 10 Å structure (eV)
1.25 V	-80.3541	-79.4658
1.50 V	-81.3837	-81.6745

Table C.4: Absolute free energies (G) of perfectly-flat case Ag_{24} for potentials higher than 1.00 V. Energetically lower points are boldfaced.

C.4 Empirical DFT Dispersion Correction

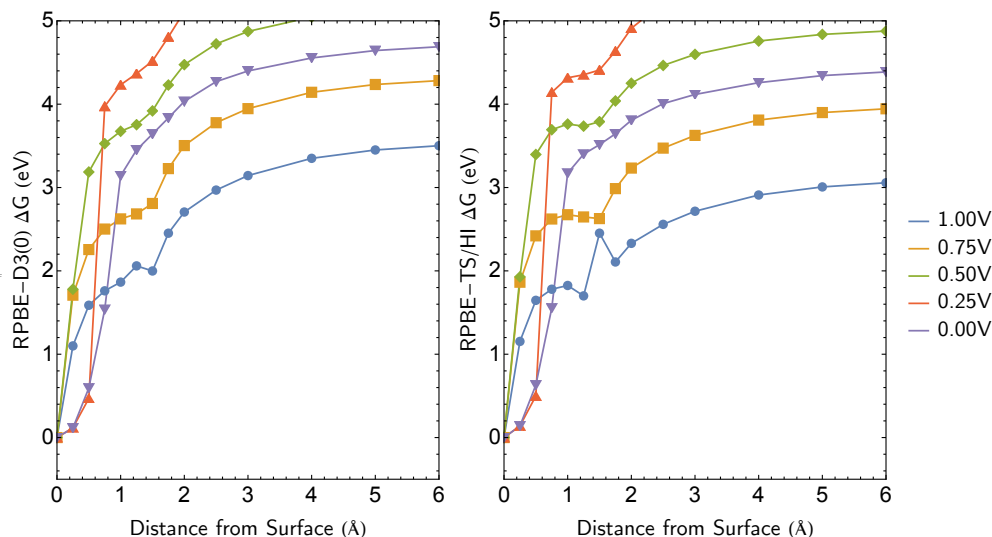


Figure C.4: Dispersion correction added free energy profiles. None of the methods presented captures the thermodynamics correctly and the free energy profiles are also erratic. (*left*) RPBE with Grimme’s D3 dispersion correction with zero damping. [92] (*right*) RPBE with Tkatchenko-Scheffler dispersion correction with iterative Hirshfeld charge partitioning. [572, 573]

Owing to its semilocal exchange-correlation functional, RPBE [88] cannot correctly capture long-range dispersion interactions such as van der Waals forces. Previous works have tested the use of adding non-local correlation [237] and utilizing a semilocal functional that directly involves the van der Waals corrections [417, 574]. We tested using empirical DFT dispersion corrections onto our calculations, specifically the DFT-D3 with zero damping (*i.e.*, DFT-D3(0)) [92] and Tkatchenko-Scheffler method with iterative Hirshfeld partitioning scheme (DFT-TS/HI) [572, 573] by appending an additional single-point electronic energy calculation on the CEP optimized structures.

Interestingly, we observe that the addition of dispersion correction errs the energies and activation barriers by predicting corrosion to be thermodynamically unfavored even for the strongest potential bias in the case of Ag_{25} , overbinding the Ag atom to the surface (Figure C.4). Noticeably,

RPBE-TS/HI is less erratic given that the corroded geometry is approximately 0.5 eV lower in energy when compared to the case with RPBE-D3(0). We suspect that this is due to the adeptness of the DFT-TS/HI correction that accommodates for the fractionally charged atomic states that are necessary for CEP protocol, compared to the DFT-D3(0) correction which only accommodates for the neutral atomic reference states. Nevertheless, both free energy curves are still inaccurate which shows that the long-range correlation between surface and Ag atom (at a dissolution limit) is overestimated. Indeed, long-range dispersion interaction should be effectively mitigated due to solvent molecules, and artificially adding this contribution estimated from gas phase structures will overcount this interaction. This observation differs from previous studies that concluded the addition of non-local correlation to be important for correct chemisorption [237] or that concluded addition of van der Waals interaction does not affect the energy profile. [417]