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of the Catalytic Activity of Transition Metal Oxides

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Abstract

The development of active and inexpensive catalysts is vital for progress in technologies related to efficient energy generation, storage, and utilization. Transition metal oxides (TMOs) make up a significant fraction of current state-of-the-art catalysts for these technologies. Density functional theory (DFT), the workhorse for computational chemistry and catalysis, can calculate the activity of catalysts, provide synthesis targets, and accelerate the discovery of active and cheap TMO catalysts. This dissertation develops DFT methods for accurately calculating and understanding the catalytic activity of TMOs.

Known electron self-interaction errors in TMO bulk oxidation energies implies reactions energies on TMO surfaces should contain similar errors. The linear response U , proposed to correct self-interaction error, was evaluated as a method for obtaining more accurate TMO reaction energies. Application of the linear response U gave unprecedented improvement in TMO oxidation energies, mixed improvement in TMO formation energies, and improved trends in TMO surface reactivity. These results motivate the continued development of linear response U for bulk and surface calculations.

The calculated electronic structure of a catalyst can be used to relate its structure and composition to its activity. Physical and chemical complexities of TMOs hinder development of useful and elucidative electronic structure models. Using the understanding of adsorption on metals as a foundation, a number of correlations between the calculated electronic structure and adsorption energy were found on TMO surfaces. These correlations led to structure-function relationships of binary, ternary, and polymorph TMOs. Methods and results used provides research directions on the continued search for new transition metal compound catalysts.

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1 Introduction

The surfaces of transition metal oxides (TMOs) catalyze both mature and up-and-coming industrially relevant chemical reactions. Mature reactions already implemented on a large scale include a large family of oxidation reactions such as carbon monoxide,¹⁻³ alcohol,⁴⁻⁶ and hydrocarbon⁷⁻¹¹ oxidation. Modern technologies currently in development that use TMOs as catalysts include hydrogen production via water electrolysis,¹² oxygen reduction in solid oxide fuel cells,¹³ conversion of sunlight into chemical energy,¹⁴ and biofuel conversion into fuels.¹⁵ A majority of these technologies are related to the efficient generation, storage, or conversion of energy.

There is a continual need for the discovery of new TMOs. For large scale, mature technologies, even incremental improvements to either the reaction conversion or selectivity can lead to massive reductions in costs. For infant technologies still in development, current state of the art catalysts are prohibitively expensive for larger scale industrial realization. Traditionally, TMO catalysts are found through trial-and-error. In the past few decades, the introduction of new quantum-chemical methods and growth of computing power has enabled the first-principles investigations of chemistry on the atomic scale. Density functional theory (DFT) is the workhorse for tackling these problems.

Figure 1.1 illustrates how DFT can accelerate the discovery of new TMO catalysts. DFT allows one to take an atomic system made of the coordinates and chemical identities (structure and composition) and calculate their complete physics (with approximations). The valuable physics for researchers studying heterogeneous catalysis are the total energy and electronic structure of the system. The total energy can be used to calculate thermodynamic and kinetic properties related to the potential activity of a catalyst. The

electronic structure can be used to relate the structure and composition of a catalyst to its activity. Together, these two calculated properties allow researchers to use DFT to screen materials as potential catalysts and accelerate the search for new TMO catalysts.

First-principles accelerated compound catalyst discovery

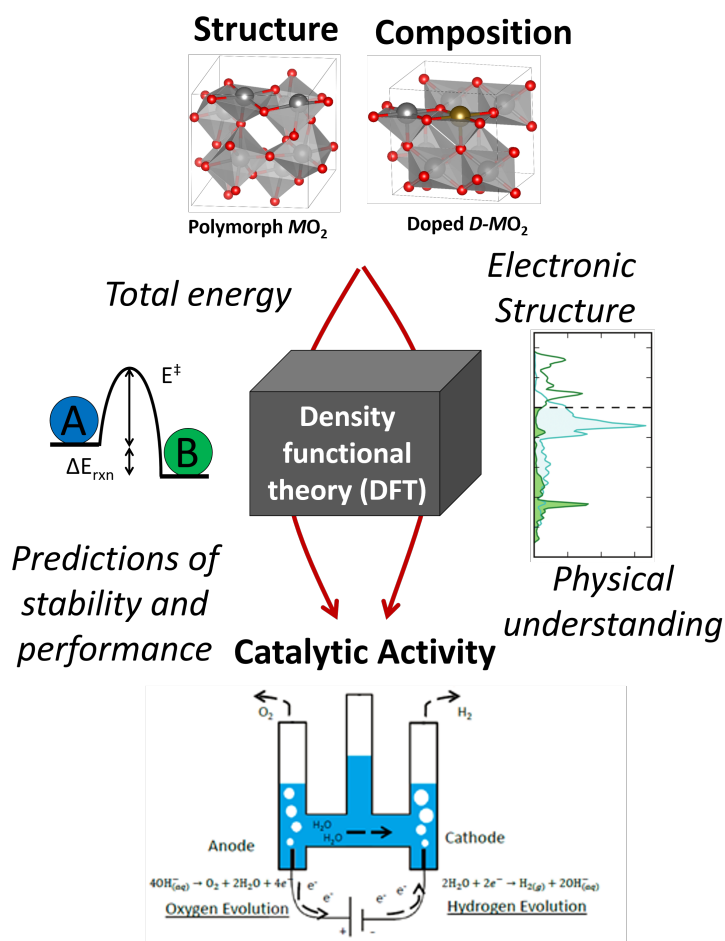


Figure 1.1: Schematic on how density functional theory (DFT) can accelerate catalyst discovery.

This dissertation advances our ability to convert the calculated total energies and electronic structure properties into useful information to accelerate catalyst design. The first half of this dissertation (Chapters 2 - 5)

is dedicated towards assessing and improving the accuracy of total energy calculations of TMOs. Chapter 2 introduces DFT, presents its limitations for calculating accurate reaction energies pertaining to TMOs, and discusses strategies used to address these limitations. In Chapter 3 a method is developed for using linear response U values for calculating accurate bulk TMO oxidation energies. The linear response U is then tested for calculating bulk TMO formation energies and surface adsorption energies in Chapters 4 and 5, respectively.

The second half (Chapters 6 - 9) of this dissertation is dedicated towards using the calculated electronic structure to build structure-function relationships of TMO catalysis. Chapter 6 reviews how researchers have used the calculated electronic structure of metal catalysts to build structure and composition sensitive models for predicting their activity. In Chapter 7, understanding of electronic structure relationships for metal catalysts is exploited to understand electronic structure relationships on binary (mono-metallic) TMOs. How the composition and structure of the TMO catalyst affect reactivity is understood in Chapter 8 and 9 through studying ternary (bi-metallic) doped and polymorph TMOs, respectively. The dissertation is concluded in Chapter 10 with a summary of the work done in this dissertation and future research directions.

2 Density Functional Theory (DFT) for Studying TMO Reactivity

2.1 Introduction to DFT: From Schrödinger’s Equation to Exchange-Correlation (XC) Functionals

As stated in the introduction, density functional theory (DFT) is the workhorse for solving for the approximate physics of quantum-chemical systems. For catalytic reactions, the primary quantum interactions of interest involve electrons and protons. To understand the limitations of DFT for accurately calculating reaction energies related to TMOs, one has to understand the source of its derivation: the Schrödinger Equation.¹⁶

$$\hat{H}\Psi = \left[\sum_i^N \left(-\frac{\hbar}{2m_i} \nabla_i^2 \right) + \sum_i^N V(\mathbf{r}_i) + \sum_i^N \sum_{i < j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi = E\Psi \quad (2.1)$$

The Schrödinger Equation, shown in Equation (2.1), is an eigenvalue problem that describes the complete physics of an atomic system with N electrons. The protons are fixed and create a potential V that the electrons interact with. Electrons also experience a potential $\sum_i^N \sum_{i < j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$ through interactions with other electrons. The $\sum_i^N \left(-\frac{\hbar}{2m_i} \nabla_i^2 \right)$ term describes the kinetic energy of the electron. The relevant quantities this equation solves for are E and Ψ . E are the energy levels of the electronic states and can ultimately be used in informing thermodynamic and kinetic models of catalytic systems. Ψ is the electronic wave function and provides the basis for understanding E values through band structures and density of states.

An exact solution to the Schrödinger Equation only exists for a system with a single electron. Numerical solutions are required for systems with more than one electron. For systems of the size that we are interested in – solids and surfaces of TMOs with adsorbates – directly solving the Schrödinger Equation numerically becomes unfeasible and impractical. The first reason is that Ψ , the variable one iterates over, is actually a function of each electron’s spatial coordinate ($\Psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N)$). Hence, numerical solutions become exponentially more expensive to solve as one increases the number of electrons. The second reason is that the electron-electron interaction term is a many-bodied problem, greatly increasing the mathematical complexity.

Density functional theory (DFT) addresses both of these issues. At its very base, DFT states that unique, ground state solutions come from not only unique $\Psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N)$ values, but also unique electron densities $n(\mathbf{r})$, which is a function of $\Psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N)$. This theory, along with a number of developments on how to recast the Schrödinger Equation, led to the Kohn-Sham Equations shown in Equations (2.2) and (2.3).

$$\left[-\frac{\hbar}{2m_i} \nabla^2 + V(\mathbf{r}) + e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + V_{XC}(\mathbf{r}) \right] \psi_i = \epsilon_i \psi_i(\mathbf{r}) \quad (2.2)$$

$$n(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \quad (2.3)$$

Equation (2.2) is a Schrödinger-like Equation for each electron, while Equation (2.3) is the conversion of individual electron wave functions $\psi_i(\mathbf{r})$ into the total electron density $n(\mathbf{r})$. The first three terms of the Equation (2.2) describes the *exact* physics of a system of non-interacting electrons and looks quite similar to the first three terms in Equation (2.1). The fact that

Equation (2.2) describes non-interacting electrons allows each electrons wave function to be solved independently, given a $n(\mathbf{r})$. Hence, instead of an intractable $\Psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N)$ with $3N$ variables, one is left with a feasible $n(\mathbf{r})$ in terms of three variables (r_x, r_y, r_z). While Equation (2.2) and (2.3) involves summations over single electronic wave function $\psi_i(\mathbf{r}_i)$, the important point is that during the iteration process of solving the equations numerically, the density $n(\mathbf{r})$ is the variable iterated over, not the entire $\Psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N)$. In addition, the electron-electron interaction is treated with a mean-field approximation, where instead of individual electron-electron interactions, each electron interacts with the entire electron density. This effectively converts the double summation in Equation (2.1) into a single integral over the electron density in Equation (2.2).

While the first three terms of Equation (2.2) accelerate the numerical evaluation by treating the electrons as non-interacting, they ignore important physics relevant to these systems – the individual electron-electron interactions. These interactions are lumped into the final term V_{XC} in Equation (2.2), which is termed the Exchange-Correlation (XC) functional. A perfect XC-functional would make Equations (2.2) and (2.3) capable of solving for the *exact* physics of any system. Hence, a major area in the field of DFT is developing accurate and inexpensive XC-functionals and is the topic of discussion – with a focus calculating TMO reactivity – in the next section.

2.2 The XC-functional: Jacob’s Ladder and Bulk Oxidation of TMOs

When performing DFT calculations, the choice of the XC-functional is typically the most important decision one has to make. The trade-offs of

different XC-functionals can be understood through Jacob’s Ladder (Figure 2.1).¹⁷

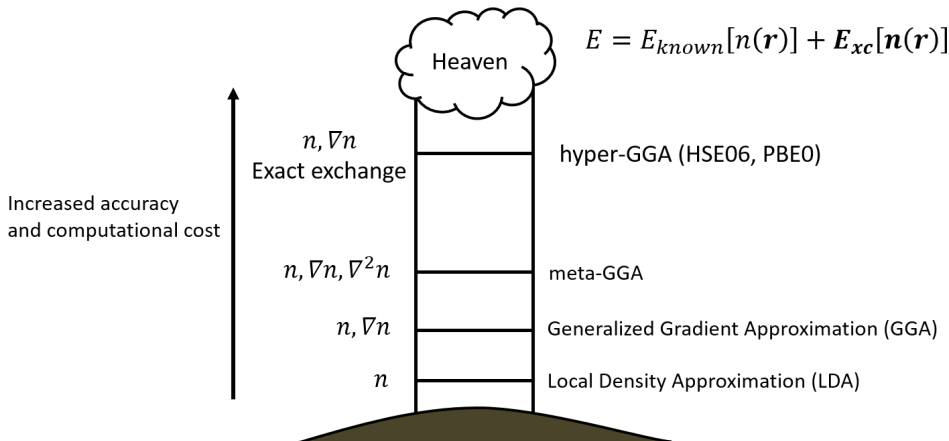


Figure 2.1: Illustration of the computational cost and accuracy trade-offs of Exchange Correlation functionals through Jacob’s Ladder.

The functionals at the bottom of the ladder contain the least physics and hence are the least accurate, but they are also the computationally cheapest to run. The Local-Density Approximation (LDA) requires only information of the electron density at the electron, while the Generalized Gradient Approximation (GGA) requires information of the electron density and the derivative of the electron density at the electron. Functionals at the top of Jacob’s ladder include more physics, but are typically too computationally expensive for large scale use. Examples of these functionals include PBE0 and HSE06, where exact exchange is mixed in with GGA-like character. One important distinction of these functionals is that they are non-local – that is, the interactions on an electron that determine its physical characteristics extend beyond its local surroundings. The cost-benefits trade-offs of the GGA XC-functional makes it one of the most popular functionals. In all of the work of this dissertation, the Perdew-Burke-Ernzerhof (PBE)^{18,19} GGA XC-functional was used.

The primary question in deciding whether the GGA is suitable for studying TMO reactivity is this: How does the functional describe charge

transfer in TMOs? Catalysis on TMO surfaces involve the making and breaking of bonds, a process that will inherently contain charge transfer. Ideally, DFT calculations of adsorption could be benchmarked with experimental measurements, but high quality adsorption on TMOs are difficult to measure experimentally.²⁰ This is partly due to the complex surface structure of TMOs that complicate the ability to directly compare computational models to real experimental systems.

A roundabout way to validate DFT XC-correlation functionals to charge transfer in TMO surfaces is by looking at bulk oxidation energies. Considering TMO are typically used in oxidizing environments with oxygen based adsorbates, adsorption on a surface and oxidation in the bulk both consist of the creation of M -O bonds. Conceptually, the formation of M -O bonds, adsorption, and oxidation both include charge transfer from the transition metal M cation to the oxygen anion. Further evidence of the chemical similarity between bulk oxidation and surface adsorption is clear from their reaction equations,

$$\Delta E_{ads} = E_{MO_x}^{surf-O} - (E_{MO_x}^{surf} + \frac{1}{2}E_{O_2}) \quad (2.4)$$

$$\Delta E_{oxi} = E_{MO_y}^{bulk} - (E_{MO_x}^{bulk} + \frac{y-x}{2}E_{O_2}), \quad (2.5)$$

where ΔE_{ads} and ΔE_{oxi} are the adsorption energy and bulk oxidation energy calculated using DFT, respectively. $E_{MO_x}^{surf-O}$ and $E_{MO_x}^{surf}$ are the calculated total energies of a MO_x slab with and without an adsorbed oxygen ion, respectively. $E_{MO_y}^{bulk}$ and $E_{MO_x}^{bulk}$ are the calculated total energies of the bulk unit cell of MO_y and MO_x . If $y > x$, then an oxidation reaction is shown. In both Equations

(2.4) and (2.5), E_{O_2} is the total energy of oxygen. Note adsorption in this case is the dissociative adsorption of oxygen.

Another advantage of validating adsorption through bulk oxidation is that both experimental and computational bulk oxidation have already been measured and calculated, respectively. A majority of bulk formation energies are stored in a variety of thermo-chemical databases and can easily be used to calculate oxidation energies.²¹ Similarly, bulk oxide total energy values have been calculated and are stored in a number of materials databases.²²

It also well known that the workhorse XC-functionals (GGA and LGA) predict inaccurate bulk oxidation and formation energies.²³ Some of these TMO bulk oxidation energies are shown in Figure 2.2. The table in Figure 2.2 shows a list of bulk oxidation reaction energies calculated using DFT with the GGA XC-functional. The right plot in Figure 2.2 relates the change in d -electrons between the reduced reactant and oxidized product of each oxidation reaction in the table with the disagreement between the experimental and DFT-GGA calculated bulk oxidation energy.

Figure 2.2 shows a number of important points related to the errors in bulk oxidation energies of 3d TMOs. First, the errors can be quite large – up to 2.5 eV per metal ion. One would like these energies to be less than 0.2 eV. Second, there is a clear positive correlation between the amount of d -electrons exchanged in the oxidation reaction and the magnitude of the error. This suggests the culprit of these errors must lie in the d -electrons.

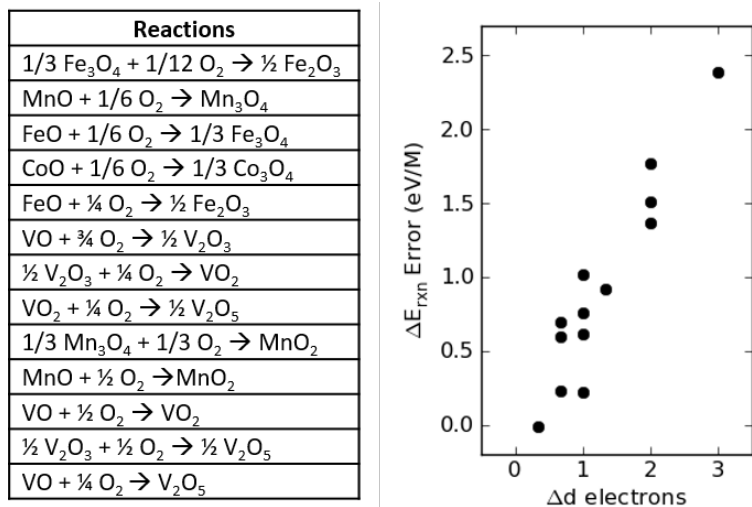


Figure 2.2: Errors in bulk oxidation reaction energies calculated using the PBE GGA XC-functional. The x -axis shows the difference in d -electrons between the reduced reactant and oxidized product.

One way to understand the relationship presented in Figure 2.2 is a lack of cancellation of error. The approximations in the GGA XC-correlation functionals lead to known errors in energetics, and researchers rely on cancellation of error for meaningful results. For example, cancellation of error of adsorption energies on metal surfaces allows one to make meaningful activity trends of metals for ammonia synthesis.²⁴ It is clear from Figure 2.2 that there is a lack of cancellation of error between two oxides with a different number of d -electrons. The next section discusses the source of this error and methods researchers have used to account for it.

2.3 Self-Interaction Error and the Hubbard U

Self-interaction error partially results from the mean field approximation of the many-bodied electron-electron interaction term ($e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r'$). When calculating the electron-electron interaction term of a specific electron, the electron density $n(\mathbf{r})$ one uses contains that specific electron and results in the

electron "seeing itself" in the electron density. One job of the XC-functional is to fix this self-interaction error, but the LDA and GGA functionals fail to do so when orbitals are partially occupied. In the case of TMOs, the d -electrons are often partially occupied. For example, the d -occupancy of FeO (Fe^{2+}) and Fe_2O_3 (Fe^{3+}) is d^5 and d^4 , respectively.

The energetic consequences of this is shown in the Figure 2.3 below, which describes an atom in contact with an electron reservoir. Exchanging electrons with this electron reservoir naturally produces changes in the system's total energy. At a fractional occupancy of electrons, such as $N+\omega$ where N is an integer and ω a fractional value, the correct total energy would be a statistical average between the total energy at N and $N+1$ electrons. This is produced by the piecewise red-dashed line in Figure 2.3.

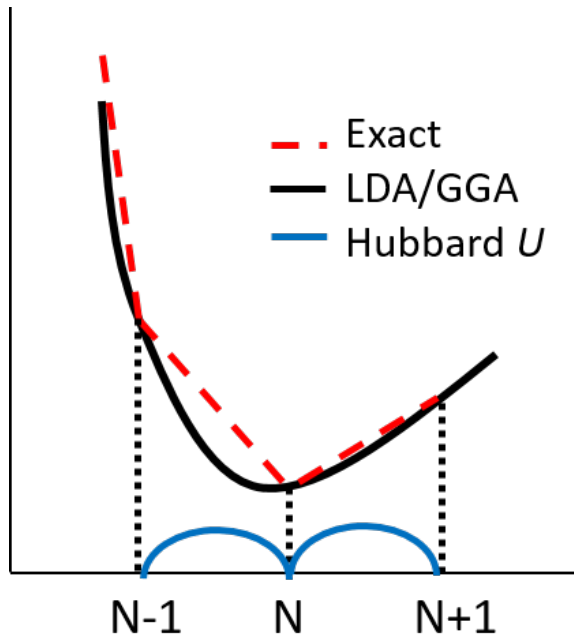


Figure 2.3: Total energy of an arbitrary atomic system as a function of number of electrons. The red dashed line is exact DFT, the black line DFT with the GGA or LDA exchange correlation functional, and the blue line the Hubbard U correction.

DFT with the LDA or GGA XC-functional instead gives a smooth curve that is correct at integer occupancies but lower in energy at fractional occupancies. This error at fractional occupancies has also been called a de-localization error due to inadequate treatment of electron correlation. While more expensive functionals can be used to bring the GGA results closer to the exact DFT, another strategy is to add a simple correction. Mere visual inspection of Fig 2.3 suggests a correction that maximizes at a fractional occupancy near half and goes to zero at an integer occupancy should bring the LDA/GGA curve nearer to the exact DFT curve.

The Hubbard U is a proposed correction that accomplishes this. The expression for the Hubbard U is shown below

$$E_U = \frac{U}{2} \sum_I \sum_i \lambda_i^I (1 - \lambda_i^I) \quad (2.6)$$

The Hubbard U correction E_U is the energetic penalty that depends on the occupancies λ of atomic orbital i on atom I . Important to note in Equation (2.6) is that while the values for λ come from a self-consistent calculations of the electron density from DFT, a Hubbard U value tunes the magnitude of the Hubbard U penalty E_U .

The caveat of this method is the parameter U that must be chosen. Furthermore is the stipulation that while the Hubbard U energy penalty E_U contains the meaningful correction one desires, E_U also contains an arbitrary energetic penalty as well through hybridization between the transition metal d -orbitals and oxygen p -orbitals. The exact nature of this arbitrary portion is elusive, but the general consensus is that total energy values calculated at different U values cannot be directly compared.²⁵ How the Hubbard U is chosen given such conditions is a major area of research.

A majority of researchers choose the Hubbard U empirically by fitting to experimental data. This is done by calculating a relevant quantity (band gap, reaction energy) at different U values and picking the U value that gives the best agreement with experiments.^{26,27} Because total energies calculated at different U values cannot be directly compared, oftentimes researchers pick an element specific U that minimizes the error across different systems.

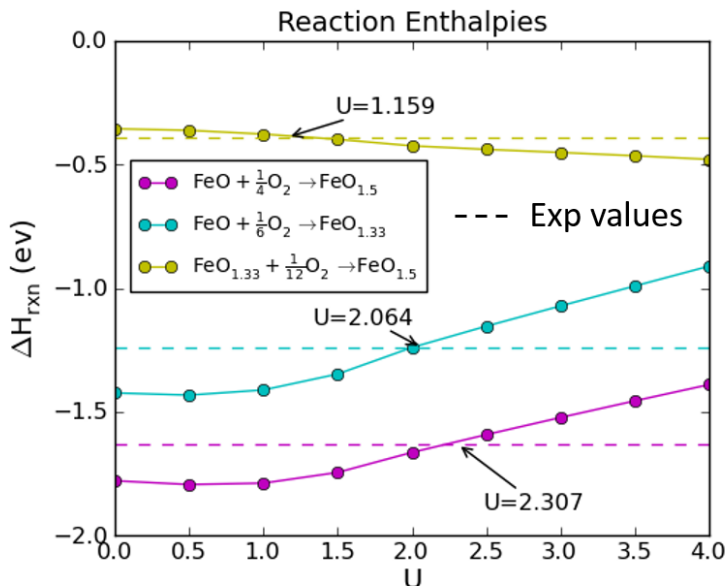


Figure 2.4: Bulk oxidation reactions involving iron oxides at different Hubbard U values.

Figure 2.4 demonstrates the primary limitation of this method. Figure 2.4 shows calculated iron oxide reaction energies at different Hubbard U values compared with experimental values. A single element specific U oftentimes cannot capture the accurate energetics of bulk oxidation reactions. Different Hubbard U values are required for different Fe oxidation reactions. Furthermore, it is not obvious whether any of these U values are transferable to adsorption on the surfaces of these reactions. It is clear from several works that the Hubbard U value required is environment

dependent,^{26,28} and ions participating in adsorption on a surface will have a different environment than being oxidized in the bulk.

In contrast to empirically determining the Hubbard U value, the system specific U can also be calculated through first principles. Fig 2.3 shows that if the curvature around the fractional occupancy is known, the Hubbard U can be chosen to produce the E_U that best corrects the spurious curvature at the fractional occupancy. This curvature can be calculated and the Hubbard U determined through a linear response method.²⁹ This method calculates Hubbard U values that produce more accurate reaction energies for a number of molecular systems,^{30,31} but has not been validated for bulk systems. In the following three chapters, the usage of the calculated linear response U is first validated through a DFT+ $U(V)$ method for the accurate calculation of bulk oxidation energies and then tested for the calculation of bulk formation energies and surface reactivity trends.

The Hubbard U also corrects certain electronic properties. In addition to errors in oxidation energies, a result of self-interaction error in TMO oxides is the delocalization of electrons. This feature of GGA is expressed in electron hole delocalization in defective oxides and the general underestimation of band gaps.^{26,32} Similar to reaction energies, the Hubbard U is often empirically fit to fix both of these errors. Chapter 3 will investigate whether the linear response U results in improved electronic properties.

3 Linear Response U for Calculating TMO Bulk Oxidation Energies

The previous chapter motivated the need for advanced electron structure methods to capture chemistry on TMO surfaces. The chapter was ended with a brief introduction into using the linear response U as a potential solution to determining a Hubbard U for capturing that chemistry. This chapter begins with a summary of the aforementioned points and introduces a DFT+ U (V) method for validating the linear response U to capture accurate bulk oxidation energies.

3.1 Introduction

The electronic and chemical properties of transition metal oxides (TMOs) is of central importance in heterogeneous catalysis, electrochemistry, photocatalysis, and sensors.^{33–35} Standard exchange-correlation functionals (LDA and GGA) in density functional theory (DFT) often fail to calculate either of these properties of TMOs accurately, which hinders our ability to identify and discover new TMOs for these applications. This failure has been partially attributed to a lack of cancellation of the self-interaction error produced by localized d -electrons.^{25,27,36} The two most common ways to account for this error is incorporation of exact exchange via hybrid functionals,³⁷ or the addition of a Hubbard U to the d -electrons of the transition metal.^{38,39} Although more accurate than DFT results, hybrid functionals have not shown significant improvement on top of the computationally cheaper DFT+ U method for calculating accurate bulk reaction energies.^{25,40,41} A majority of studies using DFT+ U for evaluating chemical properties of a large number of TMOs use an empirically

determined Hubbard U .^{23,28,42} This strategy has been successful at capturing accurate known properties but it requires experimental data. This limitation is especially relevant regarding chemical properties of surfaces, such as the adsorption energies on well defined oxide surfaces,²⁰ which are more difficult to measure than bulk properties.

In contrast to using empirically derived U values, the Hubbard U is system specific and can be calculated via a linear response method.²⁹ The linear response U has been used in studies for evaluating a number of properties of a wide variety of materials,⁴³⁻⁴⁷ but relative stabilities between TMO materials are more difficult to capture using calculated linear response U values. One reason for this is that the correction, E_U , leads to offsets in the total energy that include both the desired physical correction as well as an arbitrary contribution, shown in Figure 3.1, that makes comparisons between total energies with different U values meaningless.^{25,38,48} This difficulty is highlighted in one of the first papers employing linear response U values for the calculation of redox potentials, where it was unclear whether the reactant or product’s U values should have been used in reaction energy calculations.⁴⁸ Further studies use global U values that are averages of the linear response U values of intermediates along a reaction path, but the accuracy of this method is dependent on small differences between unique U values.^{49,50} For example, in their paper on the addition of molecular H_2 to FeO^+ , Kulik et al. found certain reaction energies and transition state barriers were more accurately described by a locally averaged U .⁵⁰ A more recent study addressed this limitation of using averaged U values by constructing a $DFT+U(\mathbf{R})$ method that takes into account derivatives of U with respect to a specific reaction path.³⁰

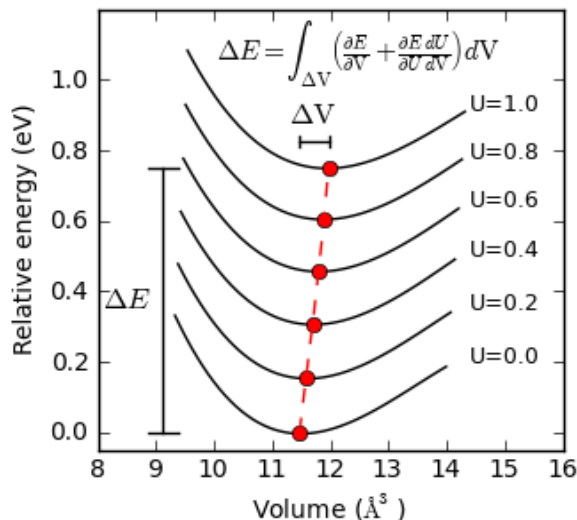


Figure 3.1: Illustration of the arbitrary offset imposed upon comparing one structure at different U values. The energy difference ΔE can be evaluated as a path integral over changing U and V space. Black curves show the energy versus volume behavior near the ground state volume of bulk Fe. The red points show the ground state volumes calculated at different Hubbard U values. The dashed red line shows a path over U and V space that is constrained to ground state structures.

In this chapter, linear response U values are used to calculate accurate electronic and chemical properties of a number of pure 3d TMOs. Calculated linear response U values leads to more accurate band gaps of most materials calculated in this chapter. A recently developed DFT+ $U(\mathbf{R})$ method for calculating potential energy landscapes of molecular reaction paths will be adapted to a DFT+ $U(V)$ method for the calculation of bulk reaction paths.³⁰ The DFT+ $U(V)$ method is then used to eliminate contributions to reaction energies due only to changes in U . A thermodynamic pathway is constructed that goes through isolated atoms and allows one to compare relative stabilities of unique U bulk transition metal oxides using the linear response U and semi-empirical DFT+ $U(V)$ method. The method is predictive and accurate for the calculation of oxidation energies of V, Cr, Mn, Fe, and Co TMOs.

3.2 Methods

All DFT calculations were performed with QUANTUM-ESPRESSO (QE).⁵¹ The exchange correlation functional used was the Perdew-Burke-Ernzerhof (PBE)^{18,19} generalized gradient approximation (GGA). The procedure for calculating the linear response U in bulk systems can be found in a previous paper by Cococcioni and de Gironcoli.²⁹ A list of the transition metal oxides, their atomic and magnetic structure, and their calculated linear response U values are shown in Table 3.1.

In QUANTUM-ESPRESSO, the projection $\mathbf{P}^I$ of the extended wave function on localized set of atomic orbitals determines the Hubbard U correction,^{52,53} and the shape of the atomic orbitals depends on how the pseudopotential was generated, such as the charge state for which the pseudopotential was generated. To show that the performance of the calculated linear response U is independent of $\mathbf{P}^I$, all calculations were performed using ultrasoft pseudopotentials from two libraries: the original QE pseudopotential library⁵⁴ and the Garrity-Bennet-Rabe-Vanderbilt (GBRV) pseudopotentials.⁵⁵ The uniqueness of each PP is highlighted in the different atomic $E_U(U)$ behavior and the calculated linear response U values (Table 3.1). While the precise source of pseudopotential dependent linear response U value is elusive, the important observation is that they generate different calculated U values. This highlights the complexity of the transferability of specific U values and emphasizes the need for calculated linear response U values, which has shown to be able to adjust accordingly to different pseudopotentials.⁴⁹

Table 3.1: All oxides used in this study along with their corresponding structure, magnetic ordering, and calculated linear response U values using both the original QUANTUM-ESPRESSO library (U_{QE}) and GBRV high-throughput PPs (U_{GBRV}) set of PPs.^{54,55} U values of compounds with inequivalent metal ions (Mn_3O_4 , Fe_3O_4 , Co_3O_4) were taken as a weighted average of the U value of each metal ion.

Compound	Crystal Structure	Magnetic Structure	U_{QE}	U_{GBRV}
VO	$F\bar{m}3m$	AFM	4.12	3.61
V_2O_3	$\bar{R}3c$	AFM	4.99	4.64
VO_2	$P2_1/c$	NM	5.14	5.02
V_2O_5	$Pm\bar{m}n$	NM	5.12	4.67
Cr_2O_3	$\bar{R}3c$	AFM	2.73	4.86
CrO_3	$C2cm$	NM	4.99	7.42
MnO	$F\bar{m}3m$	AFM	4.94	5.52
Mn_3O_4	$I4_1/amd$	FM	4.05	6.11
MnO_2	$P2_1/c$	AFM	4.78	4.20
FeO	$F\bar{m}3m$	AFM	4.10	5.80
Fe_3O_4	$F\bar{d}3m$	FM	3.72	6.07
Fe_2O_3	$\bar{R}3c$	AFM	3.47	5.21
CoO	$F\bar{m}3m$	AFM	4.89	5.86
Co_3O_4	$F\bar{d}3m$	AFM	5.43	7.44

3.3 Results and Discussion

The application of linear response U values gave improved electronic properties such as band gaps (Figure 3.2). In almost all cases when a band gap is experimentally observed, DFT without the Hubbard U predicts a smaller or non-existent band gap, and the application of U opens up and increases the band gap to give improved agreement with experimental values. Two exceptions, VO and Mn_3O_4 , are noted where the calculated Hubbard U leads to worse agreement and not much improvement, respectively. Near stoichiometric VO is difficult to synthesize, and the lack of vanadium or oxygen vacancies in our VO model likely leads to differences between the experimental and calculated band gap.⁵⁶ Studies measuring the band gap of

Mn_3O_4 are scarce, and the only experimental source found was taken of Mn_3O_4 nanorods,⁵⁷ which could be a source of the disagreement.

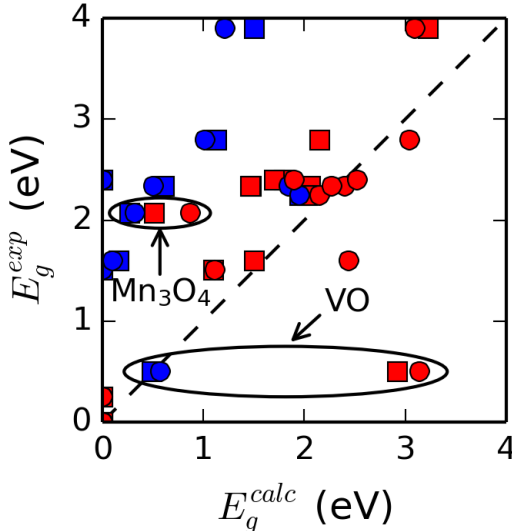


Figure 3.2: Comparison between experimental and calculated band gaps of all 3d transition metal oxides included in this study. DFT and DFT+ U results are shown by blue and red markers, respectively. Results using the original QUANTUM-ESPRESSO and Garrity-Bennet-Rabe-Vanderbilt (GBRV) pseudopotentials are shown by $\square$ and $\circ$ markers, respectively. Experimental values are taken from a number of sources.^{56–65}

In contrast to electronic properties, evaluating accurate reaction energies requires one to identify and eliminate the arbitrary offset in the total energy, shown in Figure 3.1. The ground state structures of Fe calculated at $U = 0$ and $U = 1.0$, though electronically inequivalent, both represent reference states in a thermodynamic framework. The application of U produces an arbitrary shift in the total energy of these reference points, given by ΔE that is not physically meaningful in calculating reaction energies. ΔE is composed into a path integral over the total derivative over U and V space shown in Equation (3.1). This approach, coined as DFT+ $U(\mathbf{R})$, was used in a previous study that looked at the potential energy surface of a number of dissociating diatomic molecules and a chemical reaction.³⁰ In this work, this method was extended

to bulk systems by replacing the interatomic distance of molecule $\mathbf{R}$ with the volume of a bulk unit cell V , which essentially captures the changing bond distances between atoms.

$$\Delta E = \int_V \frac{dE}{dV} dV = \int_V \left(\frac{\partial E}{\partial V} + \frac{\partial E}{\partial U} \frac{dU}{dV} \right) dV. \quad (3.1)$$

Because E depends on both V and U , the total derivative contains changes in the total energy produced by both changes in V ($\frac{\partial E}{\partial V}$) and changes in U ($\frac{\partial E}{\partial U} \frac{dU}{dV}$). Note, this derivation implies some $U(V)$ relationship. If one assumes that E is continuous with respect to U and V , the entire integral is path independent, but the contributions of each differential are not path independent. Choosing a path through U and V space that is constrained to the ground state structure (Figure 3.1), the entire arbitrary offset ΔE is contained within the ($\frac{\partial E}{\partial U} \frac{dU}{dV}$) term.

This analysis shows that if one has an appropriate $U(V)$ relationship, the physically meaningful contribution to differences in the total energies of different structures is captured by the $\frac{\partial E}{\partial V}$ term and is shown in Equation (3.2). This formalism was named the DFT+ $U(V)$ method.

$$\Delta E_{\text{DFT}+U(V)} = \int_V \frac{\partial E}{\partial V} dV \quad (3.2)$$

Theoretically, as long as one can determine a simple reaction path and derive a meaningful $U(V)$ relationship, Equation (3.2) can be used to evaluate the relative energetics of any two systems with different applied U values. To make this method practical for evaluating relative stabilities of bulk systems, which have complex crystal structures and no simple reaction paths between systems, a scheme is constructed where the total energies of all bulk systems calculated at different U values reference total energies of isolated metal atoms

and molecular oxygen at $U = 0$. This is illustrated in Figure 3.3 and derived in Equations (3.3) - (3.5) below.

$$\Delta H_{rxn} = E_{\text{MO}_y}^{U=b} - E_{\text{MO}_x}^{U=a} - \frac{y-x}{2} E_{\text{O}_2} \quad (3.3)$$

$$\begin{aligned} \Delta H_{rxn} = & (E_{\text{MO}_y}^{U=b} - E_{\text{M}_{\text{atom}}}^{U=0} - \frac{y}{2} E_{\text{O}_2}) \\ & - (E_{\text{MO}_x}^{U=a} - E_{\text{M}_{\text{atom}}}^{U=0} - \frac{x}{2} E_{\text{O}_2}) \end{aligned} \quad (3.4)$$

$$\Delta H_{rxn} = \Delta E_{\text{DFT}+U(V), \text{MO}_y} - \Delta E_{\text{DFT}+U(V), \text{MO}_x} \quad (3.5)$$

This allows the reaction path to be a simple isotropic expansion of the bulk cell, which only requires a single, one-dimensional reaction coordinate, V , in Equation (3.2). The rationale for picking $U = 0$ will be discussed in the following paragraphs.

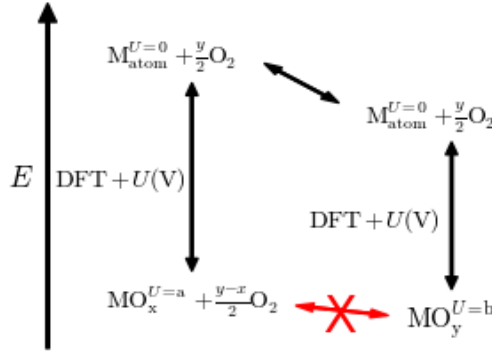


Figure 3.3: Method for calculating oxidation energies by referencing cohesive energies using the $\text{DFT}+U(V)$ method. Consider the oxidation reaction $\text{MO}_x + \frac{(y-x)}{2} \text{O}_2 \rightarrow \text{MO}_y$, where M is a transition metal. Total energies of MO_x and MO_y cannot be directly compared due to having different linear response U values. A thermodynamic cycle that goes through a common reference system to compare the relative energetics at different U values is constructed. The $\text{DFT}+U(V)$ method eliminates the unphysical contribution to the total energy produced by applying the Hubbard U .

The study by Kulik et al. gives insight on how to determine the meaningful $U(V)$ relationship³⁰ They derived a similar method for determining how the total energy of molecular systems changed when breaking a single bond. The relationship they used for $U(V)$ was the system specific, linear response calculated U value along the reaction coordinate $\mathbf{R}$, which was the length of the breaking bond. This approach yielded improved bond dissociation energies. A reasonable hypothesis is that the calculated linear response U values used in conjunction with the DFT+ $U(V)$ method should also yield improved reaction energies between different bulk systems. Many previous studies have used a linear response U derived $U(V)$ relationship for the calculation of a variety of bulk properties of $3d$ TMOs,^{44,66,67} but this study is the first to use such a relationship for the calculation of reaction energies.

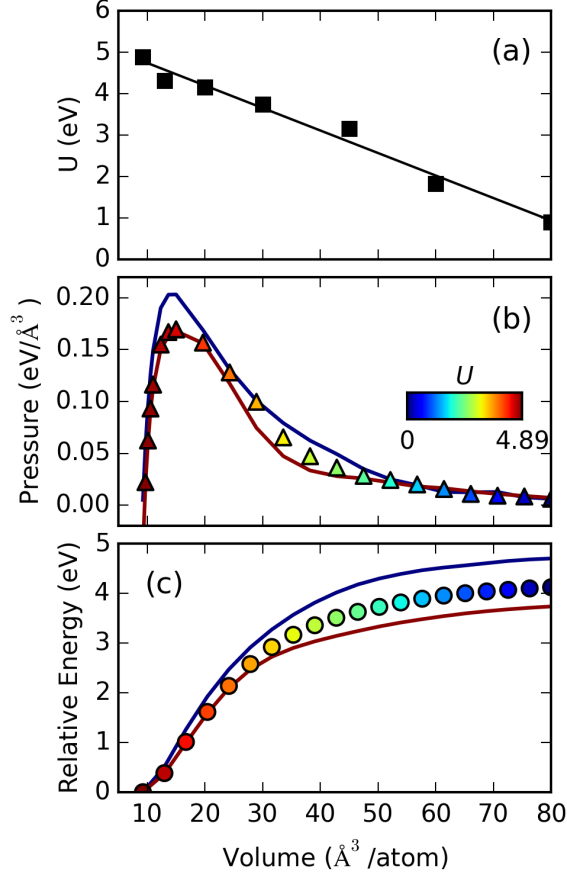


Figure 3.4: (a) The behavior of the calculated linear response U of CoO as a function of volume. (b) The negative pressure of CoO as a function of both volume using the linear response $U = 4.89$ eV of the bulk (red line), $U = 0$ eV (blue line), and the $U(V)$ relationship (Δ). (c) The potential energy surface of isotropically expanding CoO using $U = 4.89$ eV (red line), $U = 0$ eV (blue line), and the $U(V)$ relationship (Δ) calculated by integration of the pressures shown in (b). In both the $U(V)$ calculated stress and energy in (b) and (c), value of U is parametric within the calculation and is shown by the color of Δ and $\bigcirc$, respectively.

To assess the feasibility and validity of this approach, the DFT+ $U(V)$ method was first tested by calculating the reference energy of a simple bulk system. The procedure mirrors the original detailed usage of DFT+ $U(\mathbf{R})$ method on the FeO^+ diatomic molecule. The primary difference is that the system in this study is a bulk system, so that instead of interatomic distance ($\mathbf{R}$) and force ($\frac{dE}{d\mathbf{R}}$), the volume (V) and pressure ($\frac{dE}{dV}$) are the calculated

quantities. Bulk CoO was chosen, and the behavior of the total energy and calculated linear response U is shown below in Figure 3.4 (a). There is a clear trend of the calculated linear response U decreasing from the bulk value of 4.89 eV to ~ 1 eV. The linear response U of all other atoms was calculated to all be near 0 eV and less than the linear response U values of their corresponding bulk structures. Hence, $U = 0$ was chosen for all atoms as the common reference point. Because this choice is taken at the high volume limit where most bulk structures of the same element will have similar $U(V)$ behavior, it is likely that errors produced by this choice will be canceled in energy differences.

With the information of how U varies with V , a path through U and V space is used to calculate $\left(\frac{\partial E}{\partial V}\right)$ necessary to evaluate Equation (3.2). Integration along V gives the DFT+ $U(V)$ reference energy. Figure 3.4 (b) shows the negative pressure calculated by the Hellmann-Feynman theorem⁶⁸ implemented in QUANTUM-ESPRESSO using the $U(V)$ relationship shown in Figure 3.4 (a) and Equation 3.2. In Figure 3.4 (c), the negative pressures are integrated to calculate the potential surface. This gives us the DFT+ $U(V)$ energy for this specific material, which can be now used in meaningful comparisons with the total energies of systems calculated with unique Hubbard U values in equations 3.3 - 3.5.

Figure 3.4 shows that though possible, the calculation of a single DFT+ $U(V)$ reference energy is quite expensive, requiring total energy and linear response U calculations at numerous points along the isotropically expanding volume. Therefore, it would be impractical to perform the DFT+ $U(V)$ method for many systems. Figure 3.4 also shows that the DFT+ $U(V)$ reference energy lies between the cohesive energy calculated at U_{bulk} and U_0 and therefore can be written as a weighted average between the

cohesive energies at U_{bulk} and U_0 . This quantity, which we call the semi-empirical DFT+ $U(V)$ energy, is shown in Equation 3.6,

$$\Delta E_{\text{DFT}+U(V)} = x\Delta E_{\text{coh}}^{U=U_{\text{bulk}}} + (1-x)\Delta E_{\text{coh}}^{U=U_0}, \quad (3.6)$$

where x is a material specific weighting factor that can be calculated directly by the method shown above, which for CoO was found to be 0.600. Physically, x is a measure of how the self-interaction error of a transition metal produced by its d electrons is retained as its bonds are broken. Alternatively, the x value can also be fit by minimizing errors produced by the complete DFT+ $U(V)$ method for calculating bulk oxidation energies using equations 3.5 and 3.6. The set of TMOs along with their calculated linear response U values used in these fits is shown in Table 3.1.

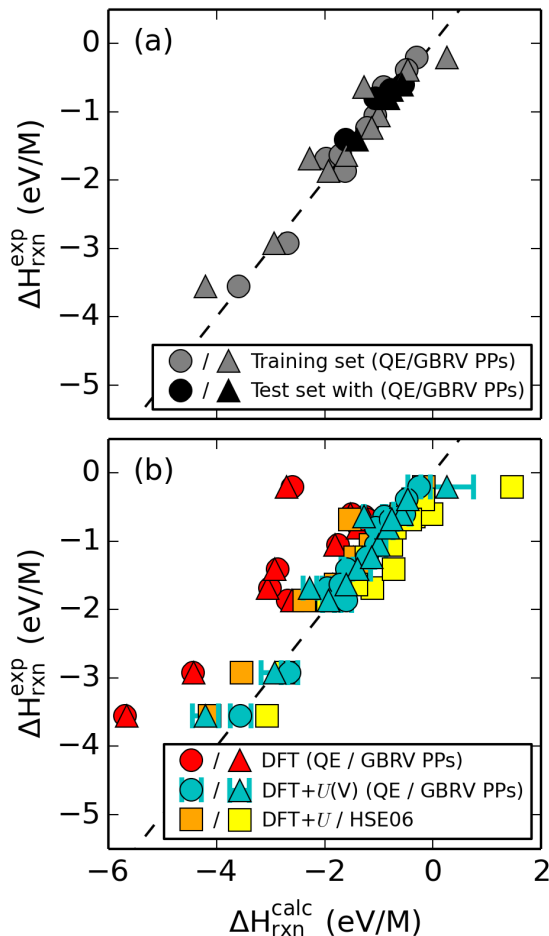


Figure 3.5: (a) Use of the DFT+ $U(V)$ on calculating oxidation energies of a test set (Cr, Mn, Co oxide reactions) with an x parameter fitted from the oxidation energies of a training set (V, Fe oxide reactions). Gray markers are training set data. Black markers are test set data. (b) All oxidation energies were calculated using a single x parameter per PP. $x = 0.599 \pm 0.053$ ($x = 0.487 \pm 0.08$) fitted to all reactions involving species in Table 3.1 with QE (GBRV) PPs and confidence intervals on the x and the calculated reaction energies. Red markers are DFT energies. Teal markers are semi-empirical DFT+ $U(V)$ energies. Orange and yellow squares are reaction energies calculated using DFT+ U with empirically determined, element specific U values and HSE06, respectively. DFT+ U and HSE06 data taken from the literature.^{22,23,40} In both (a) and (b), results calculated using QE (GBRV) PPs are $\bigcirc$ ($\triangle$).

The predictive power and accuracy of the DFT+ $U(V)$ method is now demonstrated for calculating relative stabilities of 3d transition metal oxides. This is done by calculating reaction energies of the transition metal oxides

shown in Table 3.1. Figure 3.5 (a) shows the reaction energies of a test set of reactions calculated with an x value fitted to a training set of reactions. The training set is made up of oxidation reactions involving V, Cr, and Fe oxides, while the test set is made up of oxidation reactions involving Mn and Co oxides. A low mean average error (MAE) in both the training and test set of 0.139 eV/M (0.267 eV/M) and 0.157 eV/M (0.037 eV/M) with the QE (GBRV) PPs demonstrates the predictive power of the DFT+ UV method.

Figure 3.5 (b) shows energies of all oxidation reactions calculated with the semi-empirical DFT+ $U(V)$ method at an optimized value of x compared to experiments and DFT without the application of the Hubbard U . With the QE (GBRV) PPs, the MAE using the DFT+ $U(V)$ method is 85% (79%) lower than the MAE using DFT using a fitted x value of 0.599 (0.487). Uncertainty analysis of the fitted parameter x produces confidence intervals in reaction energies that include experimental values, again demonstrating the improved accuracy using the semi-empirical DFT+ $U(V)$ method. The similar performance and x parameter of both the QE and GBRV PPs demonstrate that the improvement the DFT+ $U(V)$ method gives is independent of how the d -orbitals and occupations are defined. The excellent agreement between the overall fitted (0.599) and calculated (0.600) x value for CoO using the QE PPs further demonstrates a calculated, first-principles selection of the Hubbard U is responsible for the improved reaction energies.

It is also important to compare the DFT+ $U(V)$ method to the current widely used methods discussed in the introduction, which are namely an empirical DFT+ U method with element specific U values and hybrid functionals. Because many of these calculations have already been done, we compiled total energy data calculated using DFT+ U and the HSE06 hybrid functional³⁷ from a number of sources.^{22,23,40} The oxidation energies and

MAE values can be seen in Figure 3.5 (b) and Table 3.2. Consistent with previous work comparing empirical DFT+ U and hybrid functionals, DFT+ U outperforms hybrid functionals.^{25,40,41} We show that the semi-empirical DFT+ $U(V)$ method with a single fitted x value outperforms either DFT+ U or HSE06, which again attests the success of the linear response determined Hubbard U in correcting the self-interaction error inherent in TMO systems.

Table 3.2: Computed mean average errors (MAEs) of oxidation energies calculated using DFT, a fully empirical DFT+ U , the HSE06 functional, and the DFT+ $U(V)$ method combined with our thermodynamic framework. All reaction energies are normalized with respect to the number of metal ions involved.

Method	MAE (eV/M)
DFT (QE PPs)	0.96
DFT (GBRV PPs)	0.98
DFT+ U ^{22,23}	0.23
HSE06 ⁴⁰	0.40
DFT+ $U(V)$ (QE PPs)	0.14
DFT+ $U(V)$ (GBRV PPs)	0.20

The calculated x value for CoO using DFT+ $U(V)$ (0.600) and empirically fit x value by fitting reaction energies (0.599 and 0.487) are similar and close to 0.5, suggesting a mere average of linear response U values is sufficient. This idea has already been used in a number studies on molecular systems,^{49,50} and this chapter further validates the applicability of this method onto TMO bulk systems, which have a number of important technological applications listed in the introduction. Furthermore, the theoretical framework of referencing atomic states allows one to directly compare total energies calculated at their linear response U values and bypasses the need to re-calculate total energies at globally or locally averaged U values. Finally, there is an inherent difference between calculating reaction energies using the thermodynamic framework introduced in this chapter and

that of using a reaction specific U that was averaged between the reactant and product linear response calculated U value. By going through cohesive energies, the average is taken between the dissociative limit $U = 0$ and bulk value $U = U_{\text{MO}_x}$, not between the linear response values of the product $U = U_{\text{MO}_x}$ and reactant $U = U_{\text{MO}_y}$. It is unclear whether the two averages would produce similar results in relative stabilities.

3.4 Conclusion

In summary, this chapter shows how a calculated, linear response Hubbard U value leads to improved electronic (band gaps) and chemical (bulk reaction energies) properties of $3d$ transition metal oxides. A semi-empirical DFT+ $U(V)$ model was developed for accurately predicting relative stabilities of bulk TMOs. This model requires a minimum number of DFT calculations and incorporates the first-principles calculated linear response U . Reaction energies of transition metal oxides calculated using this method show improvement over not only DFT but also empirical DFT+ U and hybrid functional methods.

The success of the linear response U for calculating accurate bulk oxidation energies motivates its use for calculating accurate adsorption energies. Whether a metal ion is oxidized in the bulk or bonded to an adsorbate, charge transfer likely plays a key role in determining the reaction energetics. In Chapter 5, an adsorption study will be done with the linear response U . However, before performing the adsorption study, bulk formation energies of TMOs will first be presented in the next chapter.

4 Linear Response U for Calculating TMO Bulk Formation Energies

In the previous chapter, the linear response U was validated for calculating accurate bulk oxidation energies. In this chapter, formation energies using the linear response U are calculated. In addition to $3d$ oxides, $4d$ and $5d$ oxide formation energies are also calculated.

4.1 Introduction

In addition to the activity of a potential material, the stability of the material is equally important. The stability of a material determines not only its ease of synthesis but also its lifespan under reaction conditions. The simplest metric of a material’s stability is its formation energy, which is the enthalpy difference between the material and its elements in their pure form. For a TMO, it is simply the difference between the enthalpy of the TMO and the sum of the metal ion in its metallic form and gaseous oxygen.

Similar to DFT-GGA calculated TMO oxidation energies, calculated formation energies also suffer from a lack of cancellation of error.²⁷ The Hubbard U is a proposed solution to obtain more accurate formation energies, but there is still ambiguity on the usage of the Hubbard U on the total energy calculation on the metal. A majority of researchers agree the Hubbard U is not required on metallic systems. Physical and chemical properties of metals (lattice constants, cohesive energies, alloy formation energies) are accurately predicted using GGA XC-functionals.^{69,70} Adsorption energies on metals are also accurate with the GGA functional.⁷¹ Furthermore, one of the original purposes of the Hubbard U was the opening of band gaps in $3d$ TMOs, an issue not relevant in metallic systems.

In contrast, a minority view is that the success of GGA on metals comes from sufficient cancellation of error and not a perfect accounting of self-interaction error. Metal ions involved in cohesive, alloy formation, or adsorption retain their metallic nature and do not have significant changes in oxidation state. A number of studies have employed calculated Hubbard U values to study metallic systems and found more accurate calculated properties using a Hubbard U .^{29,72}

In addition to the application of U to metals, there is also ambiguity toward applying U towards $4d$ and $5d$ oxides. Electrons around the transition metal in $4d$ and $5d$ oxides are less tightly bound to their nucleus and are more delocalized than $3d$ oxides. Hence, a majority of $4d$ and $5d$ oxides are metallic, suggesting that the Hubbard U is not required. Calculated formation energies of a number of $4d$ and $5d$ MO_2 rutile species show a relatively low disagreement with experimental values.⁷³ In contrast, studies have shown that the addition of a Hubbard U improves electronic properties of PtO ⁷⁴ and IrO_2 .⁷⁵

In this chapter the linear response U is extended from $3d$ TMOs to transition metals and $4d$ and $5d$ transition metal oxides. The primary metric tested are formation energies. Relationships between DFT, DFT+ U_{calc} and DFT+ $U(V)$ calculated oxidation energies provides a simple way to test the potential accuracy of DFT+ $U(V)$ without performing fitting procedures. Using DFT calculated linear response U values, formation energies of $3d$, $4d$, and $5d$ TMOs are evaluated. In comparison to the $3d$ bulk TMO oxidation energies, errors in formation energy of all TMOs calculated using GGA are quite low. The addition of a calculated linear response U leads to improvements in formation energies of a majority of reactions, but the improvements are not as pronounced as when applied to $3d$ TMO oxidation energies.

4.2 Methods

All calculation parameters used on metals and $4d$ and $5d$ TMOs were the same as those used on $3d$ TMOs in the previous chapter. The same PBE XC-functional was used^{18,19} and all calculations were performed with both the original QE pseudopotential library⁵⁴ and GBRV PPs.⁵⁵

Table 4.1 lists the oxides used for formation energy calculations along with their crystal structures. A majority of the $3d$ TMOs were taken from the previous chapter. All $4d$ and $5d$ compounds converged to a non-magnetic ground state, and hence spin-polarization was turned off for those structures. Table 4.2 shows the crystal structure and linear response U values of the corresponding metals needed for formation energy calculations.

Table 4.1: All oxides used for calculating formation energies along with their corresponding structure, magnetic ordering, and calculated linear response U values using both the original QUANTUM-ESPRESSO library (U_{QE}) and GBRV high-throughput PPs (U_{GBRV}) set of PPs.^{54,55} U values of compounds with inequivalent metal ions (Mn_3O_4 , Fe_3O_4 , Co_3O_4) were taken as a weighted average of the U value of each metal ion.

Compound	Crystal Structure	Magnetic Structure	U_{QE}	U_{GBRV}
TiO	$F\bar{m}3m$	AFM	4.77	4.81
Ti ₂ O ₃	$\bar{R}3c$	AFM	5.02	5.03
TiO ₂	$P\bar{2}_1/c$	AFM	4.48	4.59
VO	$F\bar{m}3m$	AFM	4.12	3.61
V ₂ O ₃	$\bar{R}3c$	AFM	4.99	4.64
VO ₂	$P\bar{2}_1/c$	NM	5.14	5.02
V ₂ O ₅	$Pmnn$	NM	5.12	4.67
Cr ₂ O ₃	$\bar{R}3c$	AFM	2.73	4.86
CrO ₃	$C2cm$	NM	4.99	7.42
MnO	$F\bar{m}3m$	AFM	4.94	5.52
Mn ₃ O ₄	$I4_1/amd$	FM	4.05	6.11
MnO ₂	$P2_1/c$	AFM	4.78	4.20
FeO	$F\bar{m}3m$	AFM	4.10	5.80
Fe ₃ O ₄	$Fd\bar{3}m$	FM	3.72	6.07
Fe ₂ O ₃	$\bar{R}3c$	AFM	3.47	5.21
CoO	$F\bar{m}3m$	AFM	4.89	5.86
Co ₃ O ₄	$Fd\bar{3}m$	AFM	5.43	7.44
NiO	$F\bar{m}3m$	AFM	4.13	7.59
ZrO ₂	$Fm3m$	NM	1.69	1.76
NbO ₂	$P\bar{2}_1/c$	NM	3.00	3.03
MoO ₂	$P\bar{2}_1/c$	NM	4.20	4.51
RuO ₂	$P\bar{2}_1/c$	NM	6.09	5.89
RhO ₂	$P\bar{2}_1/c$	NM	7.29	6.93
PdO	$P4_2/mmc$	NM	6.74	6.79
WO ₃	$Pm\bar{3}m$	NM	3.27	3.28
IrO ₂	$P\bar{2}_1/c$	NM	6.20	5.63
PtO	$P4_2/mmc$	NM	5.93	5.45
PtO ₂	$P\bar{2}_1/c$	NM	6.30	5.85

Table 4.2: All metals used for calculating formation energies along with their corresponding structure and calculated linear response U values using both the original QUANTUM-ESPRESSO library (U_{QE}) and GBRV high-throughput PPs (U_{GBRV}) set of PPs.^{54,55}

Compound	Crystal Structure	U_{QE}	U_{GBRV}
Ti	hcp	3.89	3.87
V	bcc	3.88	3.59
Cr	bcc	4.28	6.02
Mn	bcc	2.81	5.94
Fe	bcc	2.29	5.22
Co	hcp	3.87	5.26
Ni	fcc	6.99	7.69
Zr	hcp	1.70	1.72
Nb	bcc	2.24	2.21
Mo	bcc	3.40	3.52
Ru	hcp	5.20	5.27
Rh	fcc	6.07	5.85
Pd	fcc	6.33	6.33
W	bcc	2.96	2.96
Ir	fcc	5.69	5.30
Pt	fcc	6.44	6.36

The equation for calculating the formation energy below using DFT total energies is shown below in Equation (4.1).

$$\Delta H_{form} = E_{\text{MO}_x} - E_{\text{M}} - \frac{x}{2} E_{\text{O}_2} \quad (4.1)$$

Similar to the last chapter, the calculated linear response U of the metal and the oxide differ. One simple way to incorporate the linear response U is to directly compare total energies calculated at different linear response U values,

$$\Delta H_{form}^{DFT+U_{calc}} = E_{\text{MO}_x}^{U=U_a} - E_{\text{M}}^{U=U_b} - \frac{x}{2} E_{\text{O}_2}, \quad (4.2)$$

where U_a and U_b are linear response calculated Hubbard U values. This is considered a meaningless quantity because it leaves in the arbitrary offset to

the total energy included in the Hubbard U , which is the motivation for the DFT+ $U(V)$ method. However, this quantity will be seen to be helpful in estimating the semi-empirical DFT+ $U(V)$ reaction energy.

As shown in the previous chapter, the semi-empirical DFT+ $U(V)$ method is one way to eliminate the arbitrary offset contained in Equation (4.2). The equations required for the semi-empirical DFT+ $U(V)$ method applied to formation energy is shown below in Equations (4.3) and (4.4), which are almost identical to Equations (3.5) and (3.6).

$$\Delta E_{\text{DFT}+U(V)} = x\Delta E_{\text{coh}}^{U=U_{\text{bulk}}} + (1-x)\Delta E_{\text{coh}}^{U=U_0} \quad (4.3)$$

$$\Delta H_{\text{form}} = \Delta E_{\text{DFT}+U(V),\text{MO}_x} - \Delta E_{\text{DFT}+U(V),\text{M}} \quad (4.4)$$

The single empirical parameter x parameter is material specific and can be calculated, but in the previous chapter this proved to be too computationally expensive to perform for many calculations. Instead, the x parameter was fit to experimental values. This is done by calculating cohesive energies at $U = 0$ and $U = U_{\text{calc}}$ for all materials and calculating material reaction energies through a difference of cohesive-like DFT+ $U(V)$ energies.

4.3 Results

4.3.1 Estimating $\Delta E_{\text{DFT}+U(V)}^{\text{rxn}}$ with $\Delta E_{\text{DFT}}^{\text{rxn}}$ and $\Delta E_{\text{DFT}+U_{\text{calc}}}^{\text{rxn}}$

While performing large scale fits of the x value to experimental formation energies is required to test the semi-empirical DFT+ $U(V)$ method, a computationally inexpensive way to assess whether *any* x value would lead to improvements in formation energies is desired. Oxidation energies of 3d TMOs from the previous chapter provide a means of doing so.

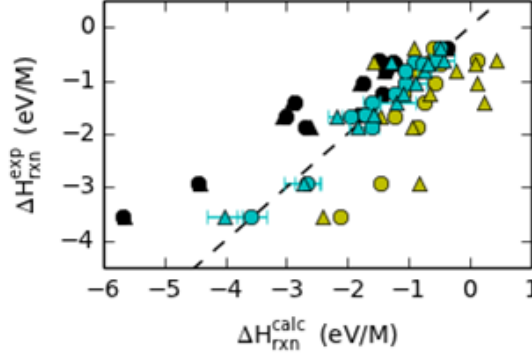


Figure 4.1: Comparison between oxidation energies of $3d$ TMOs calculated with DFT (black markers), DFT+ $U(V)$ (teal markers), and DFT+ U_{calc} (yellow markers). DFT+ $U(V)$ are calculated with optimal values of x found in the previous chapter. DFT+ U_{calc} values are oxidation energies where energies calculated at different linear response U values are directly compared (Equation (4.2))

Figure 4.1 demonstrates reaction energies calculated using the semi-empirical DFT+ $U(V)$ method with an x value near 0.6 can be estimated using DFT and DFT+ U_{calc} energies. The DFT+ U_{calc} energies are calculated by directly incorporating material specific, linear response U values (Equation (4.2)). In general, the DFT+ $U(V)$ energy lies between the DFT and DFT+ U_{calc} energy. This can be understood by noticing that the DFT+ $U(V)$ energy, reprinted below, is a weighted average of DFT energies calculated at $U = 0$ and $U = U_{\text{calc}}$.

$$\Delta E_{\text{DFT}+U(V)} = x\Delta E_{\text{coh}}^{U=U_{\text{bulk}}} + (1-x)\Delta E_{\text{coh}}^{U=U_0} \quad (4.5)$$

At $x = 0$, $E_{\text{DFT}+U(V)}$ is exactly the same as $\Delta E_{\text{coh}}^{U=U_0}$ and the reaction energy is equivalent to the DFT reaction energy. At $x = 1$, $E_{\text{DFT}+U(V)}$ becomes $\Delta E_{\text{coh}}^{U=U_{\text{bulk}}}$. Reaction energies calculated with $\Delta E_{\text{coh}}^{U=U_{\text{bulk}}}$ contain a difference in atomic energies calculated at different U_{bulk} values which is not present in DFT+ U_{calc} energies. This is shown in the derivation below.

$$\Delta H_{form}^{DFT+U(V),x=1} = \Delta E_{DFT+U(V),MO_y} - \Delta E_{DFT+U(V),MO_x} \quad (4.6)$$

$$\begin{aligned} \Delta H_{form}^{DFT+U(V),x=1} = & (E_{MO_y}^{U=U_b} - E_{M_{atom}}^{U=U_b} - \frac{y}{2}E_{O_2}) \\ & - (E_{MO_x}^{U=U_a} - E_{M_{atom}}^{U=U_a} - \frac{x}{2}E_{O_2}) \end{aligned} \quad (4.7)$$

$$\Delta H_{form}^{DFT+U(V),x=1} = E_{MO_y}^{U=U_b} - E_{MO_x}^{U=U_a} - \frac{y-x}{2}E_{O_2} + (E_{M_{atom}}^{U=U_a} - E_{M_{atom}}^{U=U_b}) \quad (4.8)$$

Comparison of Equation (4.8) and (4.2) shows the similarity between a reaction energy calculated with the DFT+ $U(V)$ method with $x = 1$ and the DFT+ U_{calc} energy. In the next section, formation energies of all oxides shown in Table 4.1 will be calculated using both DFT and DFT+ U_{calc} energies.

4.3.2 Formation Energies of TMOs using DFT and DFT+ U_{calc}

Formation energies of $3d$, $4d$ and $5d$ oxides will be presented in this section. The data will be presented for each class of oxides in similar style, and discussion will revolve around the mean average errors (MAE) of formation energies calculated using both DFT and DFT+ U_{calc} and whether the addition DFT+ U_{calc} pushes DFT values towards agreement with experimental formation energies.

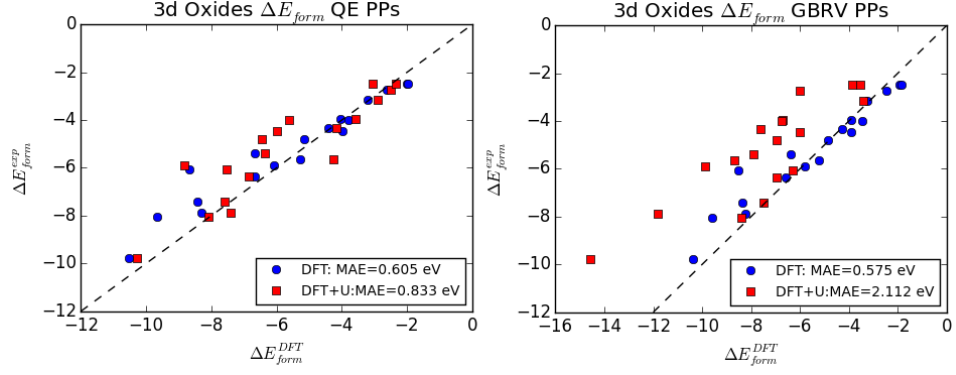


Figure 4.2: Formation energies of 3d TMOs calculated using QE (left) and GBRV (right) PPs. Blue circles are calculated using DFT (Equation (4.1)). Red squares are calculated using DFT+ U_{calc} (Equation (4.2)). All formation energies are in units of eV/M.

The formation energies of 3d TMOs are shown in Figure 4.2. In addition to the 3d oxides included in Chapter 3, Ti and Ni oxides were added. One major observation is that the errors in formation energies of 3d TMOs (0.6 eV/M) are lower by almost half of their corresponding oxidation energies (1.0 eV/M). This is most likely due to fortuitous cancellation of error.

Unlike oxidation energies, errors were less systematic for formation energies. Figure 4.1 shows that a majority of oxidation energies calculated using DFT were more exothermic than experimental values. Formation energies of 3d TMOs have less of a systematic error. Compared to experimental formation energies, more exothermic formation energies (left side of periodic table) are typically too exothermic, while less exothermic formation energies (right side of periodic table) are not exothermic enough.

Application of the linear response U has mixed results that depend on the pseudopotential used. For GBRV pseudopotentials, applying linear response U produces a strong exothermic shift of formation energies. This suggests DFT+ $U(V)$ applied to formation energies calculated using GBRV PPs would only lead to better agreement for less exothermic formation

energies (right side of periodic table). This is consistent with the understanding that late TMOs (FeO_x , CoO_x , and NiO_x) have stronger electron correlation and are more in need of the Hubbard U .²⁹ In contrast, applying the linear response U to formation energies calculated using the QE PPs does not lead to a systematic exothermic shift. Visual inspection of Figure 4.2 suggests applying DFT+ $U(V)$ will result in mixed improvement using QE PPs and larger errors using GBRV PPs.

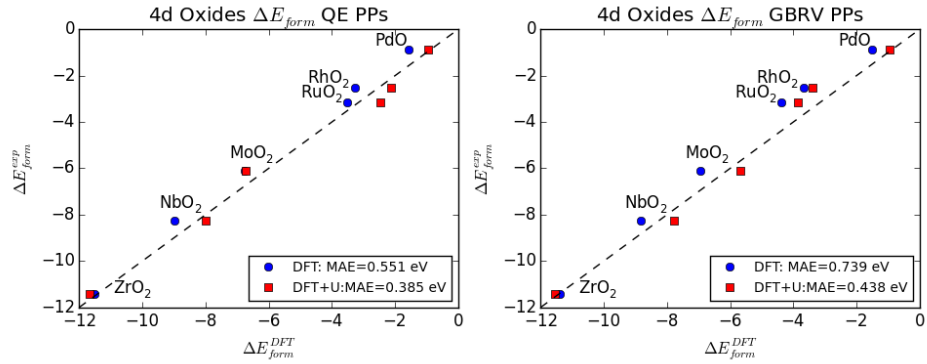


Figure 4.3: Formation energies of 4d TMOs calculated using QE (left) and GBRV (right) PPs. Blue circles are calculated using DFT (Equation (4.1)). Red squares are calculated using DFT+ U_{calc} (Equation (4.2)). All formation energies are in units of eV/M.

The formation energies of 4d TMOs are shown in Figure 4.3. The MAE of 4d TMO formation energies is similar to those of 3d TMOs. Except for ZrO_2 , all DFT formation energies are more exothermic than experimental values. For both pseudopotentials, application of linear response U leads to changes in the formation energy in the direction of the experimental formation energy. In half of the cases the experimental formation energy lies between the DFT and DFT+ U_{calc} formation energy. These observations suggest the application of a DFT+ $U(V)$ method should lead to significant improvements in 4d TMO formation energies. ZrO_2 , NbO_2 , and PdO should have consistent

improvements across both PPs, while improvements on MoO_2 , RuO_2 , and RhO_2 will be PP dependent.

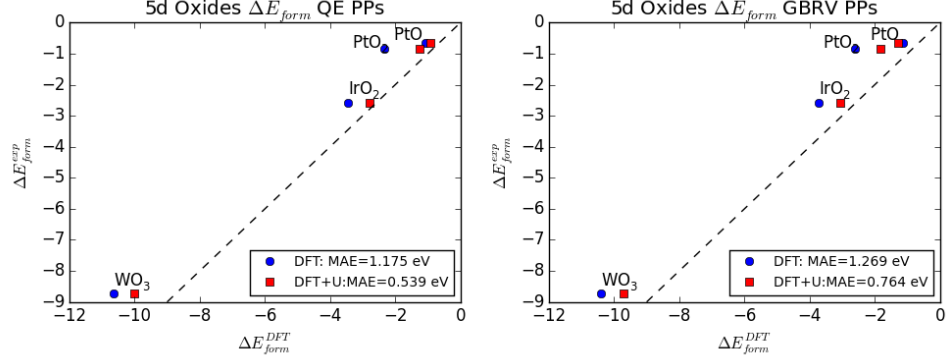


Figure 4.4: Formation energies of $5d$ TMOs calculated using QE (left) and GBRV (right) PPs. Blue circles are calculated using DFT (Equation (4.1)). Red squares are calculated using DFT+ U_{calc} (Equation (4.2)). All formation energies are in units of eV/M.

The formation energies of $5d$ TMOs are shown in Figure 4.4. The MAE of $5d$ TMO formation energies calculated using DFT are much larger than corresponding $3d$ or $4d$ MAE values. All DFT formation energies are more exothermic than experimental values. Except for PtO with the GBRV pseudopotentials, application of linear response U leads to endothermic formation energies. In none of the cases the experimental formation energy lies between the DFT and DFT+ U_{calc} formation energy. These observations suggest application of a DFT+ $U(V)$ method should lead to improvements in agreement with experimental values, but only up to the extent of an MAE of 0.539 eV/M (0.765 eV/M) using QE (GBRV) PPs. These improvements are not nearly as substantial as DFT+ $U(V)$ applied to formation energies of $4d$ TMOs.

4.4 Discussion

In addition to the $3d$ TMOs, these results motivate the application of the Hubbard U to $4d$ and $5d$ TMOs. Relative to MAE of $3d$ TMO formation energies, the high MAE of $4d$ and $5d$ TMOs suggests a similar self-interaction error is also present in $4d$ and $5d$ TMOs. However, it is not clear that the DFT+ $U(V)$ method is the best method for obtaining more accurate formation energies. While $4d$ TMO formation energies show substantial improvements with the DFT+ $U(V)$ method, $3d$ and $5d$ oxides show mixed results.

As Chapter 3 demonstrated that the linear response U leads to improvements in reactions *only* involving $3d$ TMOs, it is likely the lack of improvement of DFT+ $U(V)$ towards $3d$ TMO formation lies in the treatment of the metal energetics. This issue has been recognized in a number of studies aimed at calculating accurate TMO formation energies, and a typical solution is a correction factor applied to the metal total energy.^{28,42} Results presented in this chapter further advise a similar DFT+ U treatment of both the $3d$ metal and oxides total energy values is not appropriate.

In contrast to $3d$ TMOs, the DFT+ $U(V)$ gives more promising results for calculating formation of $4d$ and $5d$ oxides, with $4d$ showing the best potential agreement with experiments. Future work should be aimed at identifying the source of this improvement. Similar to work done in Chapter 3, bulk oxidation reactions should also be calculated of $4d$ and $5d$ TMOs with DFT+ $U(V)$. The primary difficulty of this is finding materials for oxidation reaction. A majority $4d$ and $5d$ TMOs exist in a single oxidation state. One solution is looking at other transition metal compounds. For example, the +3 oxidation state of Ru can be found in the stable RuCl_3 compound.

The consistent improvement achieved using DFT+ $U(V)$ to $4d$ and $5d$ TMO formation energies is worth noting. Compared to $3d$ TMOs, very few studies have applied a Hubbard U to $4d$ and $5d$ TMOs. A large scale study of TMO formation energies from the Ceder group applied a Hubbard U to Ag, Nb, and Mo.²³ The application of Hubbard U to $4d$ and $5d$ TMOs is still an open field of research. These results motivate further work to see whether different implementations of the Hubbard U can give improved results on $4d$ and $5d$ TMO energetics.

There are a number of systematic differences between the effect of the linear response U on formation energies of $3d$ TMOs and $4d$ and $5d$ TMOs. A majority of the $4d$ and $5d$ TMO formation energies are calculated to be too exothermic, while $3d$ TMO formation energies show both errors that are exothermic and endothermic. Similarly, the application of the Hubbard U on $4d$ and $5d$ TMOs is largely endothermic, while on $3d$ TMOs the effect – while PP dependent – is mostly exothermic.

From these results, it is not clear what the source of these differences are. The key electronic difference is that electrons on $3d$ TMOs are more localized than their $4d$ and $5d$ counterparts. Hence, many $3d$ TMOs have band gaps while $4d$ and $5d$ oxides are conductors. One consequence is the chemical similarity of the TM and TMO in the formation energy calculation. The oxidation of a $3d$ TM to a TMO in most cases results in the opening of a band-gap, while both $4d$ and $5d$ TM and TMOs are metallic. The chemical dissimilarity of $3d$ TM and TMOs might lead to errors in formation energies when applying the same linear response U treatment to both reactant and product. This chemical dissimilarity is not present in the formation energy calculation of most $4d$ and $5d$ TMOs.

4.5 Conclusions

In summary, the potential improvements to formation energies of $3d$, $4d$, and $5d$ TMOs by applying the DFT+ $U(V)$ method was assessed in this chapter. A simple way to predict the DFT+ $U(V)$ energy using DFT and DFT+ U_{calc} energies was introduced and applied to 28 TMOs. Similar magnitudes of errors for $3d$, $4d$, and $5d$ TMO formation energies imply self-interaction error identified in $3d$ TMOs is also present in $4d$ and $5d$ TMOs. A lack of improvement in $3d$ formation energies using DFT+ $U(V)$ support the consensus that similar applications of Hubbard U to both metals and oxides is not recommended. Reasonable improvement to $4d$ and $5d$ formation energies using DFT+ $U(V)$ motivate continued study of applicability of the Hubbard U to $4d$ and $5d$ oxides. An important followup study would be the calculation of oxidation energies of $4d$ and $5d$ transition metals.

5 Linear Response U for Calculating TMO Surface Adsorption Energies

As stated in Chapter 2, the primary purpose of introducing and validating a DFT+ U (V) method with bulk oxidation energies was to assess the applicability of the linear response U to surface adsorption. Oxidation is one of the primary chemistries involved during adsorption on oxide surfaces. In Chapter 3 the linear response U produced accurate bulk oxidation energies of $3d$ TMOs, which motivates its use for calculating accurate surface adsorption energies. In Chapter 4, $3d$, $4d$, and $5d$ TMO formation energies were calculated. Results from Chapter 4 motivated the extension of linear response U to $4d$ and $5d$ TMOs. In this chapter, the linear response U is employed to calculate adsorption energies of reactive species relevant to the oxygen evolution reaction.

5.1 Introduction

Density functional theory (DFT) is a first principles tool that can be used to understand catalytic processes and identify promising candidates through the calculation of kinetic and thermodynamic properties, which include formation energies, adsorption energies, and reaction barriers.^{76–79} Transition metal oxides (TMOs), a class of catalysts used in a wide variety of important chemical processes,^{33–35} have thermodynamic and electronic properties that are difficult to capture accurately using standard exchange correlation functionals (LDA and GGA).³⁶ The culprit of these inaccuracies is the self-interaction error produced by highly correlated electrons, such as the d -electrons in oxidized systems.^{25,27} The Hubbard U (DFT+ U) is the most feasible correction to account for the self-interaction error,^{38,39} but its

method of application is not trivial. The specific Hubbard U required for a given material can be empirically determined, but the experimental data required oftentimes is not available. For example, adsorption energies on well defined surfaces of oxides are typically difficult to measure.²⁰ Bulk oxidation energies can be used, but the Hubbard U values are typically reaction specific.^{27,28} In contrast, the Hubbard U can also be calculated via a linear response method,²⁹ but there have been few studies that use this method in for the calculation of catalytic properties.

One of the most studied reactions catalyzed by transition metal oxides is the oxygen evolution reaction.^{12,80} The oxygen evolution reaction (OER) is the conversion of H_2O into protons, electrons and oxygen. The high energy of protons and electrons can be stored into the chemical bonds of hydrogen, alcohols, or hydrocarbons, while pure oxygen is a widely used oxidant in chemical industries and must be separated from N_2 if acquired from air. The observed trends in kinetics of OER on different catalysts can be related to calculated chemical and electronic properties of transition metal oxides.⁸¹⁻⁸⁴ Key conclusions from these studies are that the adsorption energies of a few intermediates describe the activity trends, these adsorption energies scale with each other, and the scaling of adsorption energies produces an activity volcano with a theoretical activity limit. These conclusions were established without the Hubbard U . While a few studies have applied the Hubbard U to test cases,^{85,86} it is still not clear whether the aforementioned conclusions still apply with the application of the Hubbard U nor if the linear response U will lead to better agreement with experimental results.

In this study, DFT+ U coupled with the calculated linear response U was used to evaluate trends in activity of transition metal rutile dioxides for the oxygen evolution reaction. An atomistic thermodynamic method was applied

to relate the activity of surfaces to differences in the adsorption energies of OH, O, and OOH. The application of any U in almost all cases leads to more endothermic adsorption energies of all intermediates. These shifts in adsorption energies preserve the scaling relationships between OER intermediates calculated with $U = 0$. The combination of both observations results in relatively small shifts of all systems to the weak binding side of the OER volcano. These shifts leads to activity trends that are more consistent with experimental observations.

5.2 Methods

5.2.1 DFT Calculation Parameters

All DFT calculations were performed with QUANTUM-ESPRESSO⁵¹ with the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional.^{18,19} The core electrons were described by the GBRV library of ultrasoft pseudopotentials.⁵⁵ The kinetic energy cutoff for wave functions and the charge density were 40 and 500 Ry, respectively. For surface slabs, a $4 \times 4 \times 1$ Monkhorst-Pack grid of k -points was used.⁸⁷ All calculations were spin-polarized.

The general method for the calculation of the linear response U is described in a previous paper by Cococcioni and de Gironcoli.²⁹ For calculation of linear response U values in the bulk, perturbations up to ± 0.15 eV were applied to both the metal and oxygen in $2 \times 2 \times 2$ rutile supercells consisting of 48 atoms to ensure that interactions between the perturbations and their periodic images were minimal.

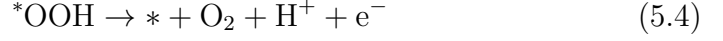
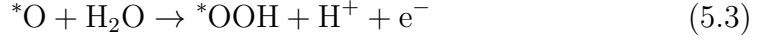
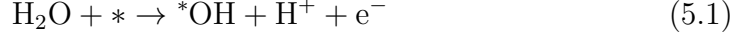
5.2.2 Structural Parameters

The equilibrium volume, cell shape, atomic positions of all transition metal dioxide rutile structures were determined by constructing a polynomial equation of state and full relaxation of the shape and atomic coordinates. Ground state magnetic configurations were calculated for all materials, taking into consideration non-magnetic, ferromagnetic, and anti-ferromagnetic orderings.

All adsorption energies were performed on the (110) surface. Because of the large number of calculations performed in this study, the (110) surface was modeled as a two layer slab with terminating hydrogen atoms on the bottom layer. A similar two layer slab has been used in previous studies of oxygen evolution on MnO_2 and IrO_2 surfaces.^{88,89} The validation of this smaller slab with respect to the typical four layer slab used in similar previous studies^{81,82,90} is discussed in the results. Figure 5.1 shows the two layer slab and four layer slab used for validation along with the adsorption site used for all calculations, which is typically called the *5cus* site.

5.2.3 Atomistic Thermodynamic Framework for Oxygen Evolution

The atomistic thermodynamic framework used to study the oxygen evolution reaction has been used before,^{81,82,91,92} so it is only briefly summarized below. The mechanism of OER is assumed to proceed through four electron proton transfer steps and the OH, O, and OOH intermediates, shown below in acidic conditions.



At constant pH and with respect to the normal hydrogen electrode (NHE), the Gibbs free energy of each elementary step is shown below,

$$\Delta G_1 = \Delta G_{\text{OH}} \quad (5.5)$$

$$\Delta G_2 = \Delta G_{\text{O}} - \Delta G_{\text{OH}} \quad (5.6)$$

$$\Delta G_3 = \Delta G_{\text{OOH}} - \Delta G_{\text{O}} \quad (5.7)$$

$$\Delta G_4 = 4.92[\text{eV}] - \Delta G_{\text{OOH}} \quad (5.8)$$

where the adsorption energy of OH, O, and OOH are as follows

$$\Delta G_{\text{O}} = E_{\text{slab},\text{O}} - E_{\text{slab}} - (E_{\text{H}_2\text{O}} - E_{\text{H}_2}) \quad (5.9)$$

$$\Delta G_{\text{OH}} = E_{\text{slab},\text{OH}} - E_{\text{slab}} - (E_{\text{H}_2\text{O}} - \frac{1}{2}E_{\text{H}_2}) \quad (5.10)$$

$$\Delta G_{\text{OOH}} = E_{\text{slab},\text{OOH}} - E_{\text{slab}} - (2E_{\text{H}_2\text{O}} - \frac{3}{2}E_{\text{H}_2}) \quad (5.11)$$

where $E_{\text{slab},A}$ is the total energy of slab with adsorbate A , E_{slab} is the total energy of the bare slab, and $E_{\text{H}_2\text{O}}$ and E_{H_2} is the total energy of H_2O and H_2 in an asymmetric unit cell. All adsorbate and gas species included previously reported zero point energy corrections.⁸²

Because each reaction step involves the transfer of an electron to the electrode, applying a potential of U volts on the electrode with respect to NHE would result in a decrease of the ΔG of each reaction step by U eV. When a potential is applied such that the ΔG for all reaction steps is less than zero, all reaction steps are considered exothermic. The potential at which this happens minus 1.23 V is considered the theoretical overpotential, η^{OER} , and is the key metric used to evaluate the activity of different catalysts for OER. The expression for η^{OER} is shown below in Equation (5.12),

$$\eta^{OER} = \text{Max}[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]/e - 1.23V. \quad (5.12)$$

The existence of scaling relationships between different reaction energies ΔG_i gives rise to a descriptor and activity volcano where either ΔG_2 or ΔG_3 is the largest reaction energy and both of their magnitudes scale with the difference between the adsorption energies of O and OH ($\Delta G_O - \Delta G_{OH}$). The details of this analysis can be found in the seminal work that originally established this atomistic thermodynamics.^{81,82} This relationship will be used to establish a similar volcano plot in the analysis in this chapter.

5.3 Results and Discussion

5.3.1 Validation of the Surface Slab Model

The investigated TMOs are shown in Table 5.1 along with their equilibrium lattice constants, magnetic structure, and calculated linear response U . The lattice coordinates and magnetic structure were then used to construct the two and four layer slabs, shown in Figure 5.1 (a). The linear response U was used when assessing the OER activity trends of the different oxides.

Table 5.1: Table of transition metal dioxides studied along with their corresponding equilibrium lattice parameters and magnetic configurations. a and c are unit cell lengths in Å, while u is the oxygen position parameter. *NM* and *FM* stand for nonmagnetic and ferromagnetic, respectively.

Compound	a	c	u	Magnetic Structure	Linear response U
TiO ₂	4.65	2.97	0.31	<i>NM</i>	4.95
CrO ₂	4.38	2.90	0.30	<i>FM</i>	7.15
MnO ₂	4.36	2.84	0.30	<i>FM</i>	6.63
NbO ₂	4.94	2.96	0.29	<i>NM</i>	3.32
MoO ₂	4.95	2.73	0.28	<i>NM</i>	4.83
RuO ₂	4.53	3.18	0.31	<i>NM</i>	6.73
RhO ₂	4.55	3.11	0.31	<i>NM</i>	5.97
ReO ₂	4.95	2.68	0.28	<i>NM</i>	5.27
IrO ₂	4.54	3.18	0.31	<i>NM</i>	5.91
PtO ₂	4.59	3.23	0.31	<i>NM</i>	6.25

The usage of the two layer surface model shown in Figure 5.1 (a) was first validated. The large amount of calculations required (over 400 adsorption energies) motivates the usage of the smaller slab. The adsorption energies of OH, O, and OOH are first calculated on both the two layer and four layer slab at $U = 0$ for all systems. Figure 5.1 (b) shows a parity plot between adsorption energies calculated on both slabs. Excellent agreement is found for OOH, good agreement for OH, and reasonable agreement for O. More importantly, Figure 5.1 (c) also shows that both sets of adsorption energies fall on the same scaling relationship. This suggests that a majority of the differences between the two adsorption energies are systematic, and that the underlying physics that results in the scaling relationships is the same for both the two and four layer slab. Following these results, all adsorption energies were calculated on the two layer slab at $U > 0$.

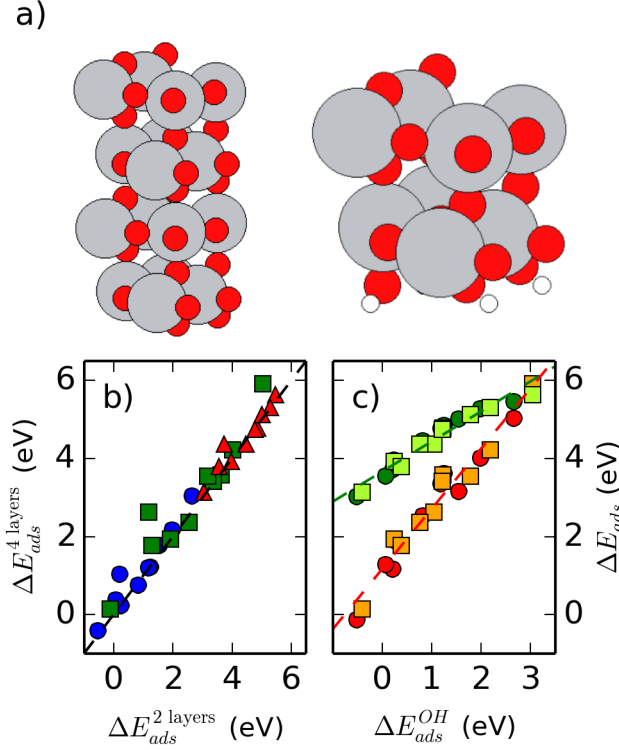


Figure 5.1: (a) The four layer rutile (110) surface (left) used to validate the usage of the two slab (right) for DFT+ U calculations of adsorption energies. Gray, red, and white spheres are Ti, O, and H atoms. (b) A parity plot between the adsorption energies of OH (blue circles), O (green squares), and OOH (red triangles) calculated at $U = 0$ on the two layer slab (x-axis) and four layer slab (y-axis). (c) Scaling relationships between the adsorption energies of OH/O (orange markers) and OOH/OH (green markers) calculated with both the two layer slab (circles) and four layer slab (squares).

5.3.2 Variation of Adsorption Energies and Scaling Relationships with Respect to U

For all materials, the adsorption energies were calculated by applying a $U = 0$ eV to $U = 8$ eV in 0.5 eV intervals. The starting geometry was taken from the relaxed structure of the calculation at $U = 0$. For brevity, results for only NbO_2 , IrO_2 , TiO_2 , and MnO_2 are discussed below. Observations for NbO_2 and IrO_2 were characteristic of early and late $4d$ and $5d$ transition metal

dioxides, respectively. For $3d$ systems, TiO_2 is a special case, and observations for MnO_2 and CrO_2 were similar.

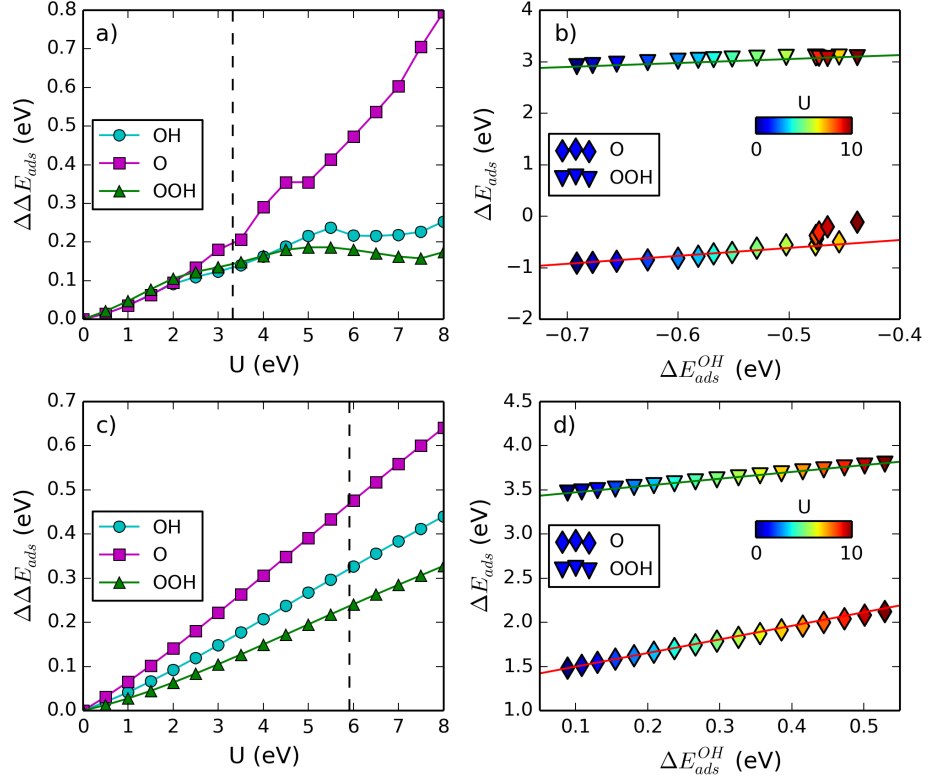


Figure 5.2: (a) and (c) show the dependence of the adsorption energies of OH, O, and OOH on U on NbO_2 and IrO_2 , while (b) and (d) show the effect of U on the OH/O and OH/OOH scaling relationships on NbO_2 and IrO_2 . In (a) and (c), the vertical dashed line shows the value of the linear response U value for the bulk oxide. In (b) and (d), the applied value of the U is shown by the color of the marker. The scaling relationships calculated at $U = 0$, shown in Figure 5.1 (c), are reproduced in (b) and (d) for the OH/O (red line) and OH/OOH (green line) offset to the adsorption energy at $U = 0$ of the particular compound for clarity.

The application of $U > 0$ had a number of systematic effects to the adsorption energies of OH, O, and OOH to the $4d$ and $5d$ TMO rutiles. These are summarized in Figure 5.2. First, the application of U results in shifts to more endothermic adsorption energies of all species on all compounds (Figure 5.2 (a) and (c)). For low U values, these shifts are

monotonic and smooth, but for high U values on early TMOs of MoO_2 , NbO_2 , and ReO_2 , they deviate from the monotonic trend at low U values. It is likely that such high values of U are not appropriate for these early TMOs. Early TMOs have a smaller occupancy of d -electrons, and therefore one would expect a lower value of U is needed to correct the self-interaction error. This is supported by the lower linear response U for the early $4d$ and $5d$ TMOs (Table 5.1). Another observation is that the calculated linear response U for all early $4d$ and $5d$ TMOs sits right at the point where the smooth, monotonic $\Delta E_{ads}(U)$ behavior breaks down. This is shown for NbO_2 in Figure 5.2 (a). This is further evidence that high U values are not appropriate for early TMOs. For late TMOs of PtO_2 , IrO_2 , RuO_2 , and RhO_2 , the changes are smooth all the way up to a $U = 8$, including their calculated linear response U values.

For $4d$ and $5d$ oxides, the U -induced endothermic changes of the adsorption energy preserve scaling relationships established at $U = 0$. This is shown in Figure 5.2 (b) and (d). This is true for all U values tested on the $4d$ and $5d$ TMOs, including high U values on early TMOs. These results further demonstrate the robustness of scaling relationships, showing that the additional physics via the Hubbard U does not lead to deviations of scaling relationships. This also demonstrates that correlations between the electronic structure and adsorption energies implied by the scaling relationships are also preserved with the addition of U . This conclusion is consistent with previous work that found similar electronic structure/activity correlations on doped TiO_2 with both DFT and DFT+ U results.⁹³

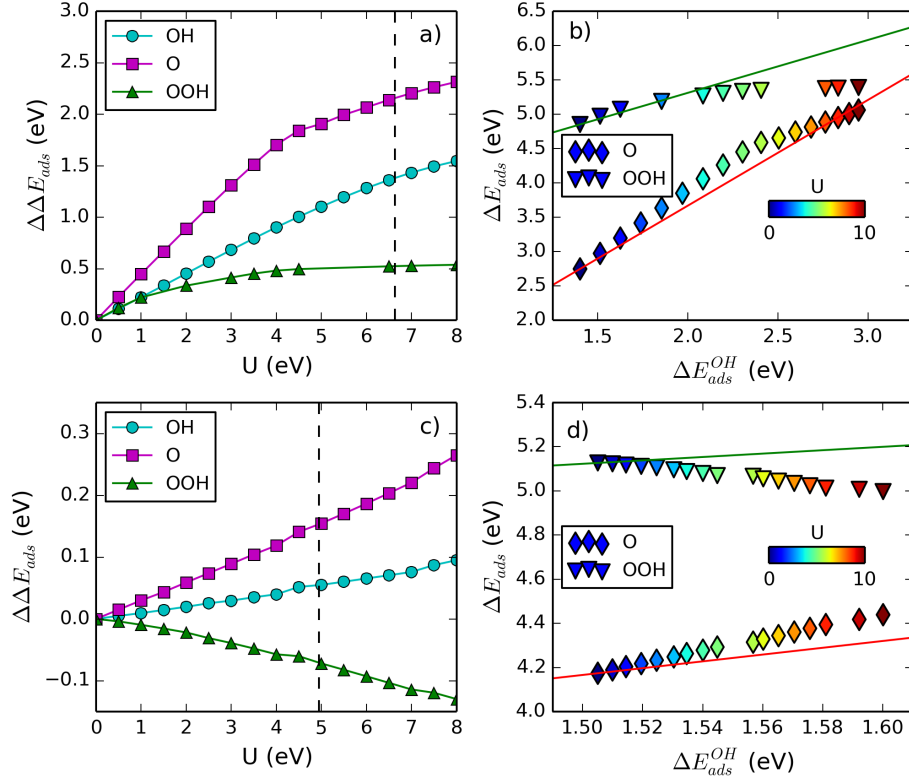


Figure 5.3: (a) and (c) show the dependence of the adsorption energies of OH, O, and OOH on U on MnO₂ and TiO₂, while (b) and (d) show the effect of U on the OH/O and OH/OOH scaling relationships on MnO₂ and TiO₂. In (a) and (c), the vertical dashed line shows the value of the linear response, calculated U value for the bulk oxide. In (b) and (d), the applied value of the U is shown by the color of the marker. The scaling relationships calculated at $U = 0$, shown in Figure 5.1 (c), are reproduced in (b) and (d) for the OH/O (red line) and OH/OOH (green line) offset to the adsorption energy at $U = 0$ of the particular compound for clarity.

In contrast to results on $4d$ and $5d$ TMOs, a mixture of results for $3d$ TMOs was found. Adsorption energies at $U > 0$ on CrO₂ and MnO₂ gave similar results to each other, with adsorption on MnO₂ shown in Figure 5.3 (a) and (b). A smooth monotonic increase in the adsorption energy accompanies increasing U values, but at some intermediate U value adsorption of OOH on the surface is no longer stable for some species, shown by the lack of change in adsorption energy for $U > 4$ eV for MnO₂. This is what gives rise to the

breaking of the scaling relationship between OH and OOH at $U \approx 4$ eV. The interpretation of the breaking of the surface-adsorbate bonds is unclear, but it is clear that even at low U values when adsorption was stable, the scaling relationships are preserved. This is consistent with results on $4d$ and $5d$ TMO rutiles.

For TiO_2 , application of U produces smooth, monotonic changes in the adsorption energy (Figure 5.3 (c)), but interestingly the change in the OOH adsorption energy is exothermic upon increasing U . This was the only adsorption energy where the addition of U produced a more exothermic adsorption energy. Also unique to TiO_2 is that the scaling relationships are not preserved with the addition of U (Figure 5.3 (d)). The relative change in the adsorption energy with respect to increasing U is also small. ΔE_{ads}^{OH} changes by less than 0.1 eV by applying a U value of 8 eV.

There is still conflicting literature on how the Hubbard U should be implemented to capture accurate thermodynamic properties of Ti oxide systems.^{26,28,41,94} These results show this is still an open issue for adsorption on TiO_2 . The Ti ion at the adsorption site of a stoichiometric TiO_2 formally has a d^0 configuration and OH, O, or OOH primarily forms bonds with the $3p$ electrons. Hence, adsorption induced changes to the electronic structure of the Ti d electrons are subtle, which is reflected by the smaller change in the adsorption energies induced by adding a Hubbard U . This electronic structure phenomenon is typical for stoichiometric surfaces of closed shell materials, such as adsorption on stoichiometric alkaline-earth metal oxides,⁹⁵ and leads to deviations in trends of both adsorption and oxygen vacancy formation energies with respect to number of electrons.^{96–98} This situation is not encountered in any other of the adsorption energies in this study.

Because of this unique change in the electronic structure caused by adsorption on TiO_2 , it was hypothesized that the application of the Hubbard U to the d -electrons of the TiO_2 after adsorption may require different treatment. The U calculated for bulk TiO_2 likely does not describe the TiO_2 with a $3p$ hole state. To resolve this special case, one might be required to calculate separate Hubbard U values of the Ti ion with and without an adsorbate and use the DFT+ $U(\text{R})$ method to calculate an adsorption energy that takes changes in U into account.³⁰ Another possibility is the requirement of application of U to lattice oxygen $2p$ states or Ti $3p$ states. A relatively high U of 6 eV applied to the oxygen $2p$ states was required to accurately capture hole states in SiO_2 doped with Al.⁹⁹

Two main conclusions can be made from this analysis of adsorption energies and scaling relationships with respect to increasing U values. With the exception of TiO_2 , where the significance of the Hubbard U to calculate adsorption on TiO_2 remains unclear, the application of U produces more endothermic adsorption energies, and these changes in adsorption energy preserve the scaling relationships established at $U = 0$. These conclusions further validate the scaling relationships and their usage for establishing models for catalytic reactions on TMOs.²⁴ The similar weakening of adsorption energies with respect to U also suggests that a majority of trend studies of adsorption on TMOs at $U = 0$ are probably valid at $U > 0$. These results also provide researchers with useful estimates on the effect of U on adsorption energies. Having established some general rules between the Hubbard U , adsorption energies, and scaling relationships, the specific application toward OER and the usage of the linear response calculated U is studied in the next section.

5.3.3 Activity Trends with Linear Response U Value

The effect of applying a calculated linear response Hubbard U to the activity trends for OER is now evaluated. Analysis is focused on the IrO_2 , PtO_2 , RuO_2 , and RhO_2 oxides in this study. Only these materials were considered for a number of reasons. First, from Pourbaix diagrams, CrO_2 , MoO_2 , NbO_2 and ReO_2 are not stable in either acidic or alkaline OER conditions.¹⁰⁰ In contrast, IrO_2 , PtO_2 , RuO_2 , and RhO_2 are predicted to be stable at acidic OER conditions and in some cases have been observed *in situ* in experimental work.^{100–102} MnO_2 was not used in this comparison for two reasons. First, it is still unclear whether MnO_2 is the active species at OER conditions. Recent studies have identified Mn^{3+} as the active species in OER.^{103,104} Second, results from the previous section point towards OOH desorption at the linear response, calculated U value. TiO_2 was not used in OER activity comparisons due to the conclusion that the DFT+ U method did not seem appropriate for an accurate calculation of adsorption energies. TiO_2 is also not a good OER catalyst.

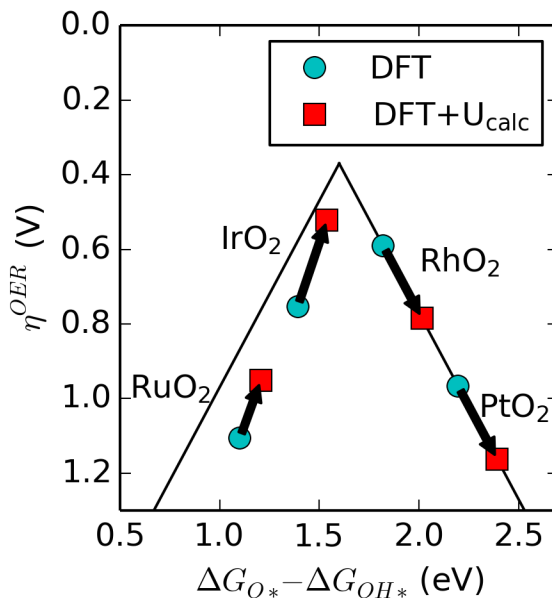


Figure 5.4: The predicted activity trends of 4d and 5d rutile dioxides calculated without (blue circle) and with (red square) the linear response U . Arrow points in the effect of applying the linear response U . The volcano is fit to the idealized scaling relationships determined in a previous paper.⁸²

Figure 5.4 shows the changes in the activity of the selected oxides as one applies the linear response, calculated Hubbard U . As expected from the observed preservation of scaling relationships, the changes in the adsorption energy produced by applying the linear response U for all species results in movement along the weak binding and strong binding legs of the volcano, but *not* changes in the activity volcano itself. Furthermore, all species are moved towards the weaker binding leg of the volcano, which is explained by the universal weakening of adsorption energies caused by applying the Hubbard U .

The combination of these two observations leads to changes in the relative ordering of activity. DFT predicts the activity trend to be $\text{RhO}_2 > \text{IrO}_2 > \text{PtO}_2 > \text{RuO}_2$. With the addition of the calculated Hubbard U the activity is predicted to be $\text{IrO}_2 > \text{RhO}_2 > \text{RuO}_2 > \text{PtO}_2$. The ordering with the addition

of the Hubbard U shows better agreement with experiments, which has been observed as $\text{RuO}_2 \approx \text{IrO}_2 > \text{RhO}_2 > \text{PtO}_2$.^{105,106} Discrepancy still exists with regard to the activity of RuO_2 with respect to RhO_2 , but the addition of U improves agreement with experimentally observed trends. IrO_2 and RuO_2 move towards the top of the volcano from the strong binding side, while RhO_2 and PtO_2 move away from the top of the volcano on the weak binding side. The combination of these two effects corrects the incorrect ordering of $\text{RhO}_2 > \text{IrO}_2$ and $\text{PtO}_2 > \text{RuO}_2$. Previous results observed a different ordering between these compounds, found to be $\text{RuO}_2 > \text{PtO}_2 \approx \text{RhO}_2 > \text{IrO}_2$, at $U = 0$. These slight differences are associated with differences in pseudopotentials, calculation parameters, and the implementation of different surface models. However, both set of results saw IrO_2 and RuO_2 on the strong binding (left) side of the volcano and RhO_2 and PtO_2 on the weak binding (right) side of the volcano. Hence, it is likely the application of the linear response U to those results should give similar improvements to those seen here, with IrO_2 predicted to be more active than PtO_2 and RhO_2 .

Though changes in ordering are observed, the absolute changes in reaction energies are relatively small. The changes in reaction energy with the application of the calculated U value was on the order of $0.2 \sim 0.4$ eV, which in no case was enough to move a species from the strong binding to weak binding side of the volcano. Hence, large scale screening studies based on correlations between adsorption energies done without and with the Hubbard U should produce similar conclusions, except perhaps near the top of the volcano.

5.4 Conclusions

To summarize, a DFT+ U study was performed on the adsorption of OER intermediates on the (110) surface of rutile transition metal dioxides. The analysis focused on changes in the adsorption energy, scaling relationships, and activity trends by applying a range of Hubbard U values in addition to the linear response, calculated U value. With the exception of TiO_2 , the application of a large range of Hubbard U values produces more endothermic adsorption energies and preserves scaling relationships established at $U = 0$. When linear response U values are applied, the relative ordering of the activity of IrO_2 , PtO_2 , RuO_2 , and RhO_2 oxides improves with respect to experimental observations. This work reveals a number of universal relationships between the Hubbard U and catalytic processes on transition metal oxides.

This chapter concludes work done in this dissertation on calculating accurate TMO reaction energies using the linear response U . A comprehensive summary of the work done up to this point along with recommendations of future work can be found in Chapter 10.1. The next four chapters are focused on using the calculated electronic structure of TMOs to understand adsorption on their surfaces.

6 The Electronic Structure and Adsorption on Metal Surfaces

As stated in Chapter 2, the DFT calculates the total energy and electronic structure of atomic systems. The total energy can be used in thermodynamic and kinetic models for predicting stability and activity. With the exception of a small discussion of band gaps of 3d TMOs in Chapter 3, the previous four chapters were exclusively focused on using linear response U methods to calculate more accurate total energies of TMOs. Starting off with an introduction to errors present in DFT in Chapter 2, these calculations were encompassed in bulk oxidation in Chapter 3, bulk formation in Chapter 4, and surface adsorption in Chapter 5. This and the next three chapters will turn our attention to the electronic structure.

Every reaction energy calculated in the previous three chapters can be understood as a difference in strength of chemical bonds. Oxide formation energies is the energetic difference between M -O bonds and M - M and O-O bonds. The oxidation of an oxide results in the conversion of an O-O bond in O_2 into an O-M bond in the metal oxide, resulting in different coordinations of M and/or the O ion in the oxide. Surface adsorption involves the creation of a chemical bond between a gas or liquid molecule and atom(s) of an extended surface.

Behind the chemical bond is the interaction of electrons between the species making the bond. The objective of this and the next three chapters is to show how these electron interactions on extended oxide surfaces can be understood through the calculated electronic structure of the oxide. This understanding elucidates the impact of structure and composition on oxide activity. This chapter will introduce the concept of the electronic structure

and review its use in interpreting adsorption on metal surfaces. Past work on metal surfaces provides a foundation to study binary (MO_x) TMOs in Chapter 7. Chapters 8 and 9 studies electronic structure relationships on TMOs with varied composition and structure through doped and polymorph TMOs, respectively.

6.1 Chemical Bonds: From Schrödingers Equation to H_2

Similar to the discussion of the source of errors in DFT for calculating TMO reactivity, understanding the electronic structure also starts with an understanding of the Schrödinger Equation.¹⁶ However, the primary focus of this chapter will not be the equation itself, but solutions to the equation and how it provides the basis of understanding what the electronic structure is and how it relates to the chemical bond.

The Schrödinger Equation is re-cast below in its simplest form.

$$\hat{H}\Psi = E\Psi. \quad (6.1)$$

Being an eigenvalue problem with boundary conditions, there are an infinite number of quantized solutions of Ψ and E for a given system. For example, the exact solution to the hydrogen atom produces a set of Ψ and E solutions that are dependent on three quantum numbers, n , l , m ,

$$\Psi(r, \theta, \phi) = R_{nl} \cdot Y_l^m(\theta, \phi) \quad (6.2)$$

$$E_{nlm} = \frac{E_{1,0,0}}{n^2} \quad (6.3)$$

$$E_{1,0,0} = -\frac{me^4}{2\hbar^2} = -1310 \frac{\text{J}}{\text{mol}}, \quad (6.4)$$

where R_{nl} and $Y_l^m(\theta, \phi)$ are complex mathematical expressions. Equations (6.2) - (6.4) are well known and are the foundation of the current understanding of molecular orbitals, but the key point is that solutions to the Schrödinger Equation of atomic systems result in multiple solutions with varying energy levels and wave-functions associated with each energy level.

The chemical bond can be understood in terms of solutions like these. One of the simplest chemical bond exists in the H_2 molecule and nicely introduces a number of concepts helpful for understanding surface adsorption. Figure 6.1 below shows an approximate solution to the Schrödinger Equation for H_2 . E is presented in a molecular-orbital energy-level diagram (a) with the corresponding solutions to Ψ for each energy level (b).

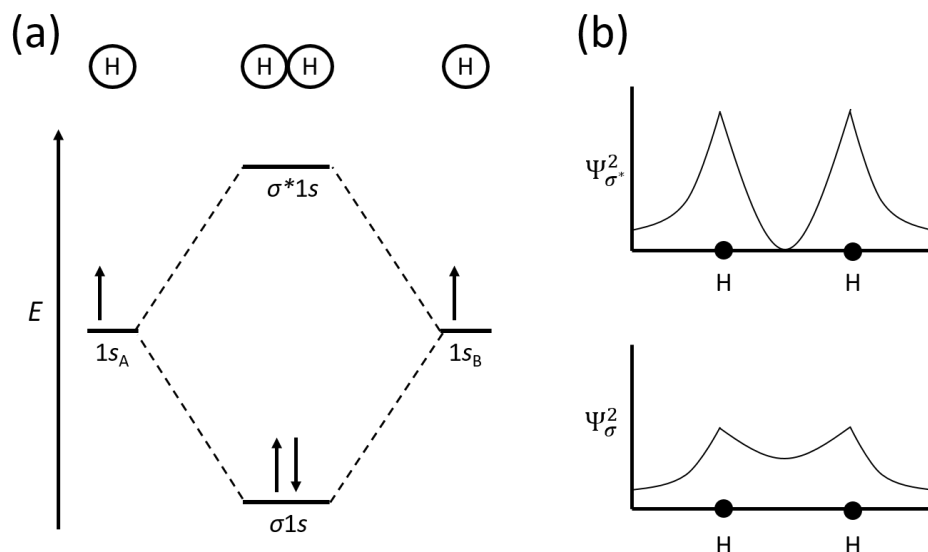


Figure 6.1: (a) Molecular-orbital energy-level diagram of the H_2 molecule. (b) Electron density of the bonding Ψ_{σ}^2 and anti-bonding $\Psi_{\sigma^*}^2$ orbital

The first key concept is that when solving the Schrödinger Equation for H_2 , the energy levels of electrons are expressed in molecular bonding and anti-bonding orbitals. These orbitals have distinct energy levels. For H_2 , the energy levels of individual atomic orbitals of H lie between that of the bonding and

anti-bonding orbitals. The concurrent formation of a bond and new molecular orbitals at distinct energy levels will be revisited in surface adsorption.

The second key concept is the occupancy of the new molecular orbitals determines the strength of the chemical bond. Due to the Pauli Exclusion principle, two electrons can occupy each molecular orbital. H_2 contains two electrons, and hence the bonding orbitals are completely filled and anti-bonding orbitals are not filled. Because the bonding orbitals of H_2 are lower in energy than the atomic orbitals of H, H_2 is more stable than $\text{H} + \text{H}$ and hence the $\text{H} + \text{H} \rightarrow \text{H}_2$ reaction is exothermic (-436 kJ/mol). This relationship between the occupancy of bonding/anti-bonding states and the formation energy of chemical bonds will be extended on in the following discussion of surface adsorption.

The final key concept is that the physical nature of the bonding and anti-bonding orbital results from the overlap between atomic electron orbitals. The electron density is related to Ψ^2 . Figure 6.1 (b) shows that the bonding orbital contains a heightened electron density in the space between the two H atoms. This heightened electron density results from an overlap of electron density between the 1s orbitals of H. Understanding the relationship between orbital overlap in Figure 6.1 (b) and electron energy levels in Figure 6.1 (a) will be instrumental in understanding not only surface adsorption, but how structure and composition affect surface adsorption.

The next section will use these concepts to explain adsorption on metal surfaces. For emphasis, the three concepts built from understanding solutions to the Schrödinger Equation with respect to H_2 are given again below.

- Chemical bonds in molecules are made up of bonding and anti-bonding orbitals at different energy levels than non-bonded species

- The filling of the bonding and anti-bonding orbitals determine the strength of the bond
- Overlap between atomic orbitals determine the energy levels of the bonding and anti-bonding orbitals

6.2 Metal Surfaces and Adsorption

The goal of this section is to take the three key concepts introduced in the previous section and use them to explain adsorption on a metal surface. The electronic structure of the surface will be introduced first. The formation of the surface-adsorbate bond will then be explained by recasting the previous three concepts.

Similar to H, the adsorbate electronic structure is made up of discrete electronic states. This is due to the discrete number of electrons in the adsorbate molecule. In contrast, an extended surface of a catalyst has a large number of atoms and hence a large number of states. Hence, it is more helpful to think of the electronic structure as made up of *bands*, which are a collection of states. As the number of atoms approaches infinity, this band becomes a continuous collection of states. Figure 6.2 below shows this concept of discrete states becoming bands. The lower right graph in Figure 6.2 (b) is called density of states (DOS) and is the primary way the electronic structure will be represented in the following three chapters.

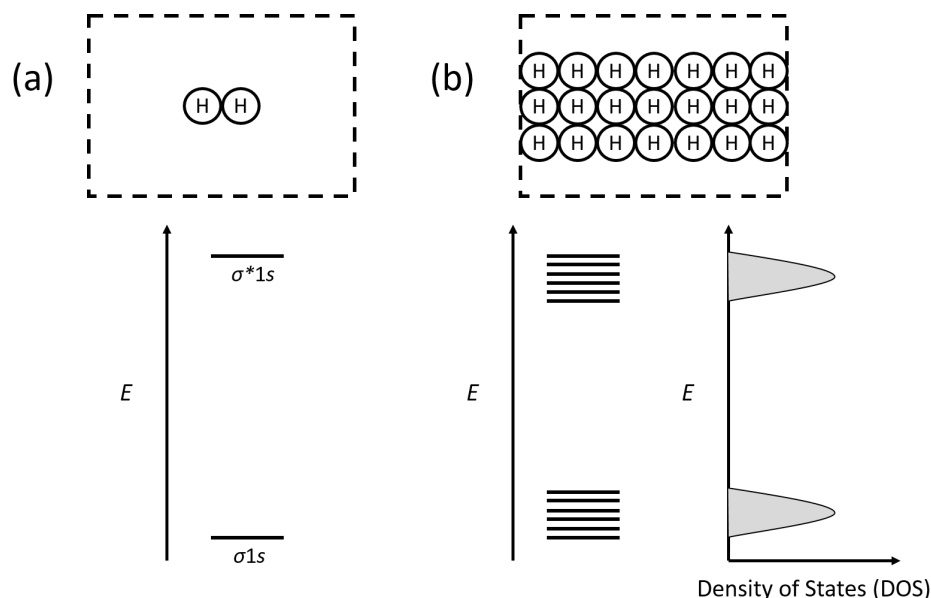


Figure 6.2: Comparison between (a) electronic states in isolated molecules versus (b) bands of states in periodic materials. Lower right shows a density of states, which is a common way to express the collection of discrete electronic states that make up a band of states.

The primary electrons involved in bonding for the TM are the valence electrons. For alkaline and alkaline earth metals, these are the s electrons. For transition metals (TMs), which is the focus of this chapter, both the s and d electrons participate in bonding. For an extended surface, these s and d electrons form s and d bands. From solutions to the Schrödinger Equation, the s electrons have a higher principal quantum number n than the d electrons. The s electrons are less tightly bound to the TM and are further away from nucleus than d electrons. The s -band has a broad distribution of electronic states, while the d -band has a sharper distribution of electronic states.

The interaction of bands of electrons on a surface with discrete electronic states of an adsorbate can be understood within the context of molecular bonding discussed in the previous section. This is shown in Figure 6.3 below. Similar to the creation of bonding and anti-bonding orbitals in molecules, bonding and anti-bonding bands are created. The energy levels of these new

bonding and anti-bonding bands will be different than the original energy levels. The electronic states of the adsorbate will interact with both the transition metal s and d electrons. First, low energy occupied bonding bands and unoccupied anti-bonding bands are created through interaction of adsorbate states and the s band of the TM. These bonding bands are typically lower in energy than the adsorbate electronic states and serve to stabilize the surface-adsorbate bond. For TMs, the contribution of the s -band to bonding is relatively constant.

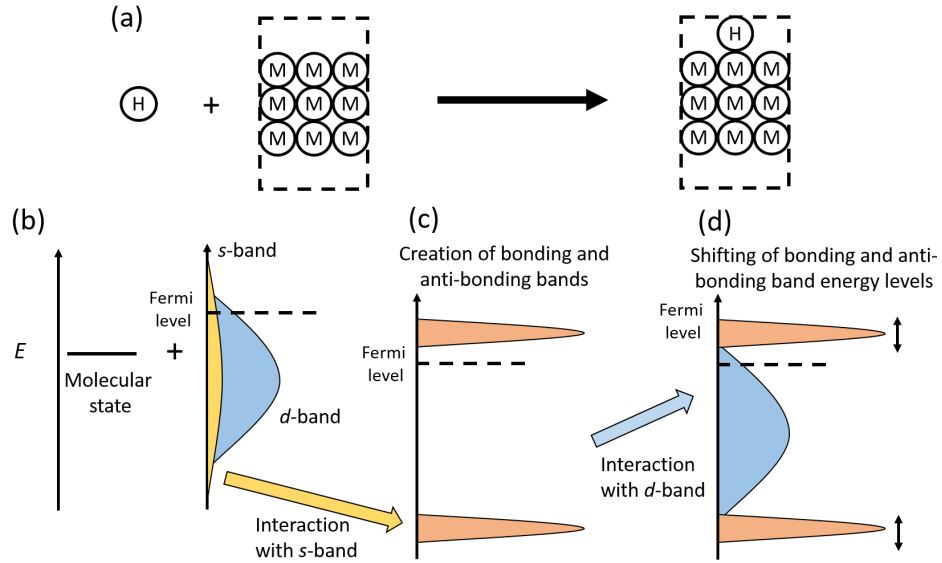


Figure 6.3: Electronic structure of adsorption on metal surfaces. (a) Creation of surface-adsorbate bond. (b) Initial electronic states of adsorbate and transition metal surface. (c) Creation of bonding and anti-bonding bands through interaction of adsorbate state and transition metal s -band. (d) Shifting of bonding and anti-bonding bands through interaction with transition metal d -band.

Due to the constant contribution of the s -band, the transition metal d -band differentiates adsorption on different TMs. Because the d electrons are more tightly bound to the TM than the s electrons, they are less involved in forming bonds with the adsorbate and instead serve to destabilize the bond through electron-electron repulsion. The hybridization between the d -electrons and

bonding and anti-bonding orbitals results in shifts to the energy level of the bonding and anti-bonding bands.

The significance of energetic shifts of the bonding and anti-bonding bands to adsorption strength can be understood in terms of the Fermi level of the system. The Fermi level is the energy of the occupied state with the highest energy. All states with energies below/above the Fermi level are occupied/unoccupied. The Fermi level energy itself depends on the number of electrons in the system, so it is conventional to set all electron energies with respect to the Fermi level. All figures presented in the next three chapters will have the Fermi level set at zero. The Fermi level has been indicated with a dashed line in Figure 6.3.

The Fermi level provides information on the occupancy of different electronic states. If the states are interpreted as bonding and anti-bonding bands, then the Fermi level gives information on whether a surface-adsorbate bond is a strong or weak bond through determining which bands are occupied. Occupied bonding/anti-bonding bands result in a strong/weak bond. Hence, the presence of the *d*-band induces energetic shifts in the bonding and anti-bonding band that changes their filling, thereby changing the surface-adsorbate bond strength.

To summarize, the three key concepts introduced in the previous section to molecular bonding can be recast to explain surface adsorption below.

- Adsorption on surfaces is made up of bonding and anti-bonding bands at different energy levels than the isolated adsorbate and surface
- The filling of the bonding and anti-bonding bands, given by their energy levels with respect to the Fermi level, determines the strength of adsorption

- Overlap between the TM *s*-band and *d*-band and adsorbate orbitals determines the energy levels of the bonding and anti-bonding bands

6.3 Relating the Structure and Composition of a Metal to its Activity

The *d*-band is key towards understanding how a metal catalyst's composition and structure determine its activity. The *d*-band shape and position determines the filling of the adsorbate bonding and anti-bonding bands; the composition and structure of the catalyst determines the *d*-band shape and position. In short, analysis of relationships between chemical properties (adsorption) and electronic properties (DOS) of catalysts elucidates structure-property relationships. A comprehensive review of how these ideas have advanced the field of catalysis on metals is beyond the scope of this dissertation. Instead, a number of seminal works unearthing how structure and composition determine the activity of metal catalysts will be briefly summarized. Many of the ideas implemented in the next three Chapters have a foundation in the following work done on metal catalysis.

The initial discovery of the *d*-band model came in 1995 by Hammer and Nørskov.¹⁰⁷ A majority of the explanations in the previous section are based off this paper. Along with relating adsorption to electronic structure, Hammer and Nørskov clarified how moving up/down and left/right among the transition metals alters both the *d*-band and adsorption strength. A key observation was the relationship between *d*-electron count and *d*-orbital radius of the metal to its *d*-band properties.

A number of studies immediately following the seminal work of Hammer and Nørskov were those investigating how the structure of the catalyst impacts activity. Strain on metal surfaces induces changes to the $M - M$ surface bonds

and results in changes to d -orbital overlap and d -band shape.¹⁰⁸ Natural defects to a metal surface results in adsorption on edge, corner, and kink sites. These sites are geometrically different due to different coordination environments around the active site. A change in the coordination of a metal ion results in either thinning or broadening of the metal d -band.¹⁰⁹ These alterations to the d -band shape results in changes to the filling of bonding and anti-bonding bands of chemical bonds during adsorption. This structure-sensitivity has been exploited to synthesize more active catalysts through shape and size specific engineering of nano-particle catalysts.^{110,111}

Composition has also been investigated using the d -band model. Initial studies differentiated the ensemble and ligand effect of creating an alloy catalyst.¹¹² The ensemble effect arises from changing the metal ions *at* the adsorption site. Adsorption sites with an ensemble effect often have multiple unique surface metal atoms forming bonds with the adsorbate, such as a three fold hollow site with two Pd atoms and one Cu atom. The ligand effect is the change in the chemical properties of specific metals at an adsorption site by changing its neighbor metal ions *outside* of the adsorption site. These neighboring don't directly interact with the adsorbate but modify the adsorption site metal atoms. One popular example of the ligand effect is in core-shell catalysts: the activity of the metal ion at the shell is altered through electronic interactions with metal ions in the core. These electronic interactions can be understood through the d -band model. Changes to the d -orbital overlap from dissimilar metal ion neighbors create changes to the position and shape of the d -band.¹¹³ Similar to structural modifications, composition induced changes to the d -band result in changes to the filling of bonding and anti-bonding bands of chemical bonds during adsorption.

These electronic structure relationships have led to elucidating and useful physics based models. This is done by relating the d -band properties to known properties of the metal ion. As eluded in the above discussion, one of the key electronic properties of the metal ion is the d -orbital radius. The d -orbital radius is tabulated in solid-state tables and has simple relationships with the calculated d -band shape and position. These relationships can be exploited to make electronic structure models that provide a catalyst's activity given its structure and composition.¹¹⁴ A few studies have used these models to screen catalysts for the oxygen reduction reaction and sulfur tolerance.^{115,116}

A similar effort is currently underway on TMO catalysts but is still in its infancy. There is currently no model that has as much universal usage and utility on oxides as the d -band model has for understanding structure-function relationships on metal catalysts. A number of complexities of the atomic and electronic structure make this endeavor difficult. These complexities stem from adding oxygen to the TM lattice. The mere presence of oxygen in a metal lattice adds a plethora of complexities to both modeling and understanding the atomic and electronic structure. This will be discussed and addressed in the rest of this dissertation. One major difficulty of inaccurate reaction energies due to oxidation state changes was already addressed in Chapters 2 to 5.

The next three chapters use the understanding built in Sections 6.1 and 6.2 and the road map paved on metal catalysts presented in this section to study electronic structure relationships on TMO catalysts. Chapter 7 builds an understanding of adsorption on $3d$ TMO catalysts upon the foundation of metal catalysis through exploiting their structural similarities of FCC metals and rock-salt monoxides. Results from studying $3d$ TMOs provides a number of important guidelines in the continued study of TMOs in the following

chapters. The influence of changes to binary TMOs composition and structure to activity is studied in Chapters 8 and 9, respectively.

7 Surface Chemical and Electronic Properties of Binary TMOs

The previous chapter introduced the idea of using the calculated electronic structure (DOS) as a means to understand structure-function relationships on transition metal catalysts. It also hinted at the atomic and electronic complexities present when studying TMOs. One strategy of studying a new, complex system is to start with a system that is understood quite well. An obvious starting point are transition metals themselves. This chapter takes advantage of TM and TMO systems with common structural motifs to use knowledge of adsorption on TMs to understand adsorption on TMOs

7.1 Introduction

In the past decade, the use of density functional theory (DFT) has accelerated materials discovery of new metal alloys for numerous catalysis applications.^{77,115–118} One recent strategy developed to lower computational costs is to create predictive models that connect the known chemical properties of metals to the electronic structure through the use of DFT calculations.¹¹⁹ This allows one to perform a coarse screening of hundreds of alloy systems for desirable properties.^{115,116} The physical accuracy of these models is based on the ability to connect the electronic structure and reactivity through simple descriptors such as the *d*-band width and center, which one can connect to known chemical properties of the metal.^{114,119} A similar strategy should also accelerate computational materials design of

metal oxides as well, but there still lacks transparent and useful electronic descriptors that have the same predictive power that the d -band center and width do for metals. However, recent work on transition metal oxides suggest these descriptors should exist. Linear scaling relationships of adsorption energies on transition metal oxides suggests that some electronic structure feature is parametric within these relationships.^{82,120} The discovery of simple electron counting rules for adsorption energies on oxides also suggest a hidden electronic structure correlation.⁹⁷ Finally, a few studies have been able to directly relate properties of the oxygen p -band^{83,121} and bulk transition metal e_g and d -band to reactivity on perovskites.^{96,122}

To understand relationships between oxide electronic structure and their reactivities, this chapter draws inspiration from a seminal paper by Gelatt et al. on the theory of bonding of transition metals to non-transition metals¹²³ and a recent DFT paper that validated these results for metal rutile dioxides.⁷³ They recognized that there were two primary steps to transform a bulk transition metal into a compound with a non-transition metal: lattice expansion of the transition metal and then subsequent bonding with the non-transition metal. They were able to describe the formation energy of the compound as a sum of an energy cost of expansion and an energy gain of making bonds between the transition metal and non-transition metal. Finally, they connected physical and electronic structure properties to explain formation energy trends. A similar approach should lead to greater understanding of the relationship between the electronic structure and reactivity on oxide surfaces.

In this chapter, the relationship between the reactivity and electronic structure of oxides is elucidated by using structural perturbations to connect the reactivity of an oxide surface with that of a metal. This analysis was

performed on six first row transition metals (Ti, V, Mn, Co, Ni, Cu) constrained to the fcc structure and their corresponding rocksalt monoxides (TiO, VO, MnO, CoO, NiO, CuO). Two simple structural perturbations can convert the fcc to the rock-salt structure: isotropic expansion and an insertion of an interpenetrating oxygen fcc lattice. The intermediate structure then is the expanded metal fcc lattice that has the same lattice constant as its respective oxide. By calculating adsorption energies on the metal, expanded metal, and oxide, the adsorption energies on the monoxide are decomposed as a sum of the adsorption energy on the metal and the change in the adsorption energy caused by both expanding and oxidizing the metal lattice. Changes in the structure and composition of the surface are connected to changes in the electronic structure, which ultimately can be related to the reactivity. To interpret reactivities from the electronic structure, the adsorption energy on both metals and oxides was found to have the same correlation with the oxygen p -band center. Expansion of the lattice causes either a narrowing or a complete breakdown of the d -band that typically leads to a weaker surface-adsorbate bond. Oxidation of the lattice produces a downward shift in the surface d -band which can result in stronger adsorption if the surface d -bands and adsorbate p -bands are degenerate in energy. These conclusions shed new insight into not only possible electronic descriptors but also their physical origins.

7.2 Methods

All calculations were performed with the Vienna Ab-initio Simulation Package (VASP).^{124,125} The core electrons were described by the projector-augmented wave (PAW) method^{126,127} and the exchange correlation functional used was the Perdew-Burke-Ernzerhof (PBE)^{18,19} generalized

gradient approximation (GGA). The Kohn-Sham orbitals were expanded with plane-waves up to a 520 eV cutoff. All k -points were represented on Monkhorst-Pack grids.⁸⁷ For bulk calculations, an $8 \times 8 \times 8$ grid k -point grid was used for metals and a $7 \times 7 \times 7$ for the expanded metals and oxides. Calculations of adsorption energies on all surfaces were done with a $7 \times 7 \times 1$ k -point grid with 10 Å of vacuum, and the density of states (DOS) analysis on surfaces were done with a higher ($12 \times 12 \times 1$) k -point grid to ensure a fine quality DOS. Surface d and p band centers (E_d) were done via the first moment of the projected DOS about the Fermi level (E_f) and is expressed as

$$E_d = \frac{\int \rho E dE}{\int \rho dE} \quad (7.1)$$

All bulk and slab calculations were done including spin-polarization in both ferromagnetic and antiferromagnetic states. The lattice constants used for slab construction were determined from the bulk calculations. Slab calculations were done with symmetric cells with six metal layers. The middle two layers were held at fixed positions, while the outer four layers (two for each side) were allowed to relax in the direction perpendicular to the surface. For calculations including relaxation, the force criteria was set to 0.05 eV/Å. Images of the bulk and surface structures as well as the adsorption sites can be seen in Figure 7.1. The adsorption energies normalized per O atom are calculated according to the equation below:

$$E_{ads}(eV/O) = \frac{1}{2}(E_{slab,O_2} - (E_{slab} + E_{O_2})) \quad (7.2)$$

In Equation (7.2), E_{slab,O_2} and E_{slab} are total energies of the symmetric slab with and without an O atom adsorbate on both sides, while E_{O_2} is the total

energy of an oxygen molecule calculated in an asymmetric box. The 1.36 eV correction for the overbinding energy of the oxygen molecule found by Wang *et al.* was used.²⁷

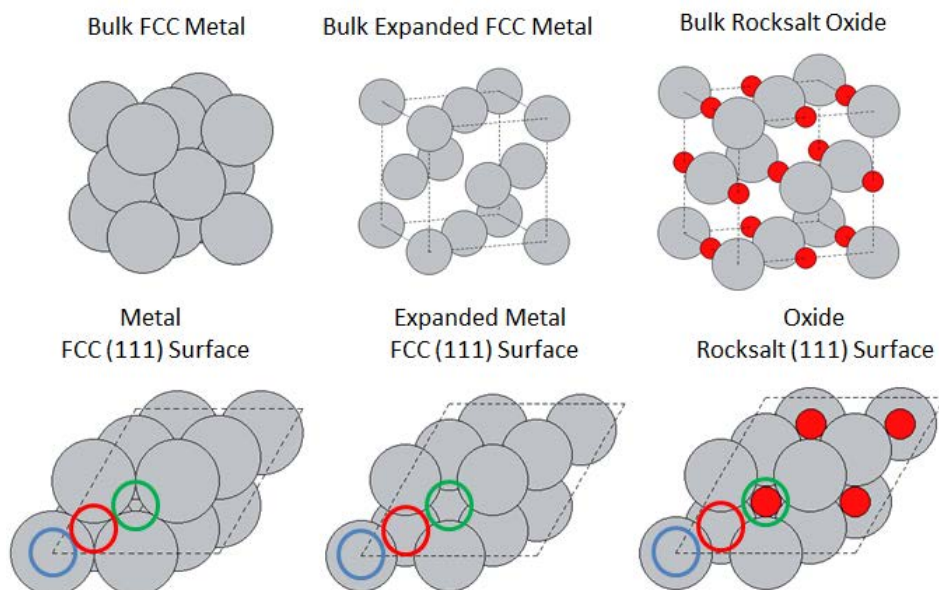


Figure 7.1: Shows the structural transformations to go from an FCC metal to a rocksalt oxide. Figure also shows corresponding surface transformations on equivalent surfaces of the two materials. Blue, green, and red circles show the top, fcc, and hcp, respectively, adsorption sites used in this study.

7.3 Results and Discussion

Calculations on the bulk unit cells were first performed to find the equilibrium lattice constants and most stable magnetic ordering for metals and oxides. The equilibrium structures and stable magnetic orderings were then used to calculate adsorption energies on metal and oxide surfaces on the top, fcc, and hcp adsorption sites. From Figure 7.2 (a), the adsorption trends on oxides and metals on the different adsorption sites appear similar. As the number of *d*-electrons increases, the adsorption energies decrease, which is consistent with a number of previous works that looked at trends in adsorption energies across first row transition metal oxides.^{96,97}

To understand the contributions to the trends in the adsorption energies on the oxides, adsorption energies were calculated on an intermediate structure: the expanded fcc metal lattice. This expanded lattice has the same volume per metal atom as the oxide but lacks the lattice oxygen. To study the change in the bonding between the adsorbate and this artificially expanded lattice, only the adsorbate was allowed to relax in these adsorption calculations. By calculating adsorption energies on this structure, the adsorption energy on the oxide can be deconvoluted as a sum of the original metal adsorption energy, a change in the adsorption energy caused by expanding the metal lattice, and a change in the adsorption energy caused by oxidizing the expanded lattice. For the rest of this chapter, these changes in the adsorption energy will be referred to as the "expansion energy" and the "oxidation energy". Figures 7.2 (b)-(d) show that the trends in expansion and oxidation energies are consistent across the different adsorption sites, and that the expansion energy is generally positive (weakens the surface-adsorbate bond) and the oxidation energy is generally negative (strengthens the surface-adsorbate bond). The magnitude of both energies rises as one goes from the beginning to the middle of the first row transition metals and then decreases going to the late first row transition metals.

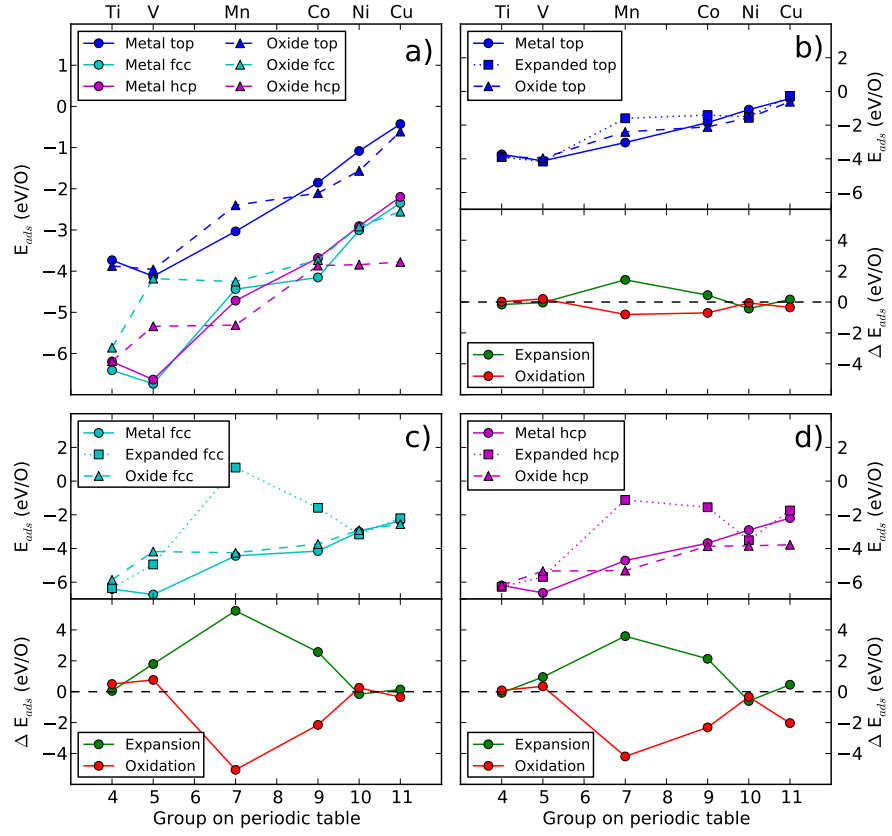


Figure 7.2: a) shows the adsorption energies on metals and oxides on all the sites. b), c), and d) show the contributions of expansion energy and oxidation energy to the adsorption energies on oxides. The expansion energy is the change in the adsorption energy caused by expanding the metal, while the oxidation energy is the change in the adsorption energy caused by oxidizing the expanded metal. The top halves of b), c), and d) show the absolute adsorption energies on the metal, metal with the expanded lattice, and oxide, while the bottom halves show the change in adsorption energy caused by lattice expansion (green) and by lattice oxidation (red).

The primary value of doing the calculations on the expanded metal lattice is that it allows one to systematically connect changes in the atomic structure and composition to changes in the electronic structure, which can ultimately be related to the adsorption energy. However, a method of interpreting changes in the electronic structure to changes in the adsorption energy is required. The

original d -band model provides a starting point, which related the position of the adsorbate bonding and anti-bonding states (in this case, the oxygen p -states) to the position of the center and width of the d -band.¹⁰⁷ These original results suggest that one way to interpret changes in the adsorption energies is by directly looking at the average energy of the adsorbate states.

Figure 7.3 (a) first shows this method is valid for metals and consistent with the d -band model. Furthermore, Figure 7.3 (b) shows the position of the adsorbate p -states can also be used to understand the adsorption energies of not only the metals, but also the expanded metals and oxides as well. The fact that the same electronic structure correlation can be used for both metals and oxides is quite extraordinary and suggests similar bonding mechanisms on both surfaces. The adsorption energies on expanded manganese and cobalt are two outliers. The reason for these outliers is that the manganese and cobalt expanded lattice is so large that the nature of the adsorbate surface bond resembles more individual molecular bonds, and the simple calculation of the average p -state energy is insufficient to capture the reactivity.

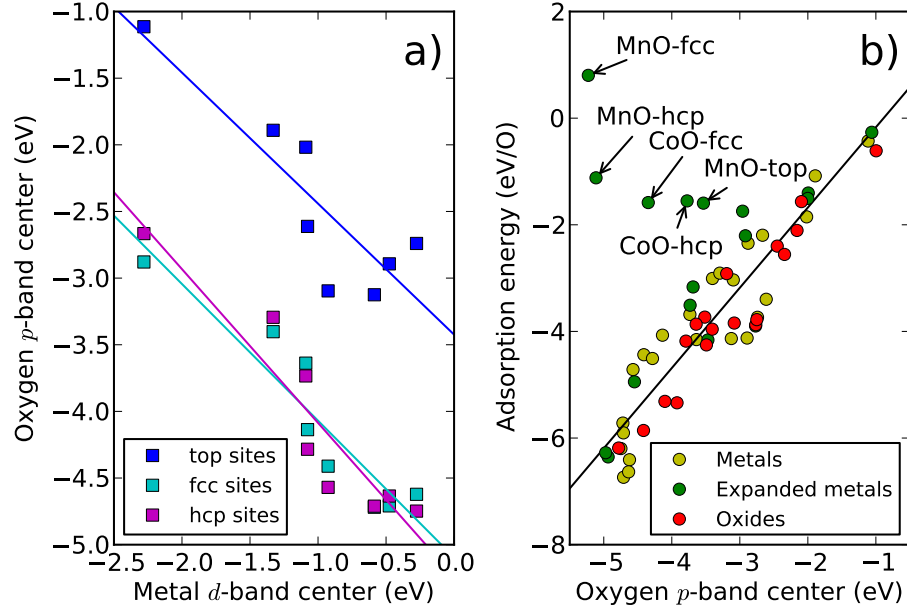


Figure 7.3: a) shows the correlation between the surface projected d -band center and the average energy of the adsorbate p -states on the top, fcc, and hcp adsorption sites on metals. b) shows the correlation between the adsorption energy and the average energy of the adsorbate p -states on metals, expanded metals, and oxides on all sites.

Now that the electronic structure has been correlated with the adsorption energy on all surfaces, the next step is to interpret the relationship between changes in the atomic structure and composition going from a metal to an oxide (expansion and oxidation) to changes in the adsorption energy. The starting point of this analysis is adsorption on metals, which is easily understood through the original d -band model. This is seen in the figures of the surface atom projected, electronic structure of early (Ti), mid (Mn), and late (Cu) transition metals with an adsorbate on the fcc site (Figures 7.4 (a), (c), and (e)). In Figure 7.4 (b), (d), and (f), expanding the lattice produces changes in the d -band that shift the position of the oxygen p -band. On early transition metals (Figure 7.4 (a), (b)), expanding the lattice narrows the d -band and produces a down shift of the d -band center, which raises

(weakens) the adsorption energy. These results are consistent with past studies that calculated strain induced changes in the adsorption energy on early transition metals.¹²⁸ For mid transition metals (Figure 7.4 (c), (d)), the expansion of the lattice is so large that the d -band splits into bonding and anti-bonding parts. The large increases in the adsorption energy are associated with a high amount of tensile strain (26% for Mn) and a lack of hybridization between surface d -states and adsorbate p -states. On late transition metals (Figure 7.4 (e), (f)) expansion of the lattice also narrows the d -band, but has opposite effects on the adsorption energy between Ni and Cu.

The effect of strain on the adsorption on late transition metals has previously been explored in numerous articles. The main conclusion is that narrowing of the d -band produces a shift down in energy, which decreases (strengthens) the adsorption energy. This is consistent with the result on Ni and inconsistent with this result on Cu.¹⁰⁸ To explain this discrepancy, the tensile strain applied on Ni and Cu are 19% and 17%, which is up to four times higher than the tensile strain used in past studies on Cu.¹⁰⁸ Similar to mid transition metals, it is apparent that the high amount of tensile strain pushes up the adsorbate p -band bonding states to higher energies and also lowers the amount of hybridization between the surface d -band and adsorbate p -states, both of which would result in a weaker bond and higher adsorption energy.

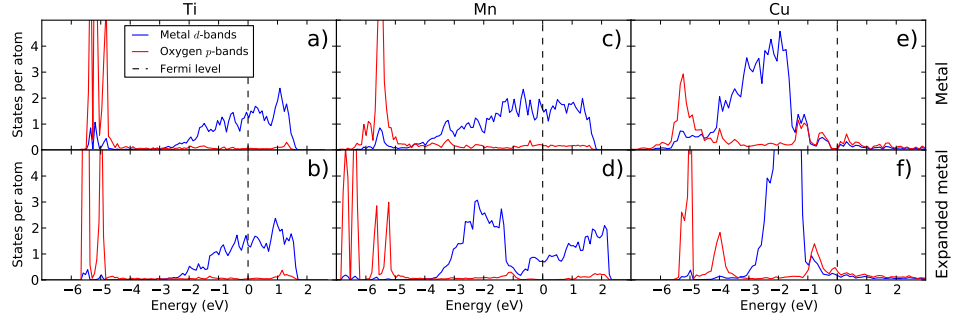


Figure 7.4: a) and b) show the density of states of Ti and expanded Ti with oxygen adsorbed at the fcc site. c) and d) show the density of states of Mn and expanded Mn with oxygen adsorbed at the fcc site. e) and f) show the density of states of Cu and expanded Cu with oxygen adsorbed at the fcc site.

Following expansion, the lattice goes through oxidation, which is an insertion of an interpenetrating fcc oxygen lattice and the formation of six metal-oxygen bonds per metal. This bonding is apparent through the hybridization of the lattice oxygen p -states with the metal d -states to create hybridized states at lower energies (Figure 7.5). The position of these new hybridized states indicates how much energy can be gained by an oxygen bonding to an under-coordinated surface. In addition, the adsorbate bonding states are shifted up in energy with respect to their energies on the expanded lattice. Whenever the energy of the adsorbate bonding states on the expanded lattice are degenerate in energy with the new hybridized lattice metal-oxygen states, the surface-adsorbate bond is strengthened through additional hybridization between adsorbate p -states and surface d -states. This is most prominent for mid (Figure 7.5 (c), (d)) and late transition metal oxides (Figure 7.5 (e), (f)). Furthermore, as one goes from mid to late transition metal oxides, these new hybridized bonding states move up in energy, thereby lowering the amount the surface-adsorbate bond can be strengthened through oxidizing the lattice. In contrast to mid and late transition metal oxides, the early transition metal oxide hybridized states are

lower in energy than the adsorbate bonding states, which led to little hybridization between the adsorbate bonding states and surface states (Figures 7.5 (a), (b)). The lack of hybridization in addition to the upshift in energy of the adsorbate states led to an overall increase (weakening) of the adsorption energy on early transition metal oxides.

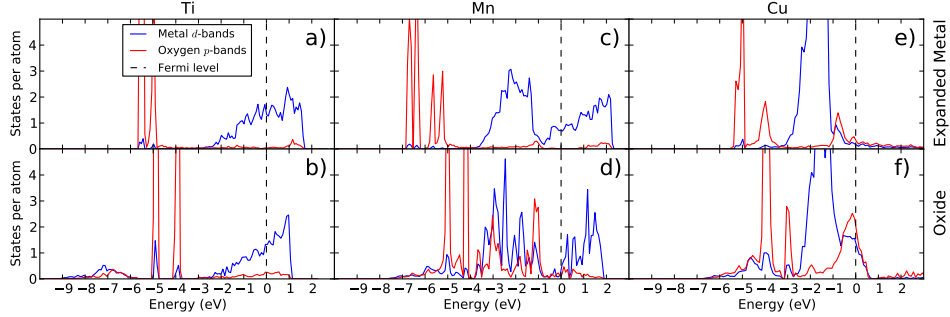


Figure 7.5: a) and b) show the density of states of expanded Ti and TiO with oxygen adsorbed at the fcc site. c) and d) show the density of states of expanded Mn and MnO with oxygen adsorbed at the fcc site. e) and f) show the density of states of expanded Cu and CuO with oxygen adsorbed at the fcc site.

7.4 Conclusions

To summarize, key features of oxide electronic structure that determine the strength of the dissociative adsorption energy of oxygen have been identified. This was done through performing structural perturbations to transform a fcc metal into a rocksalt monoxide, tracking changes in both the adsorption energy and electronic structure and how they relate to changes in the surface atomic structure and composition. Expanding the metal lattice narrowed and produced shifts in the d -band, and the effect on the adsorption energy depended on both the magnitude of the volume expansion and the position of the metal on the periodic table. Oxidizing the lattice allows the surface to form stronger bonds with the adsorbate if the energies of the bulk bonding d -band states created through hybridization with bulk oxygen

p -states are degenerate with the adsorbate p -band states. The position of the bulk bonding d -states formed through oxidizing the lattice also determines the strength of this effect. To interpret these relationships between the electronic structure and adsorption energy, a common correlation between the energies of the adsorbate p -bands and adsorption energy for both metals and oxides was found. These results elucidate the mechanism of adsorption and provide insight into the relationship between electronic structure and reactivity on oxide surfaces.

8 Surface Chemical and Electronic Properties of Doped Ternary TMOs

The previous chapter explored electronic structure relationships on binary TMOs. However, real catalysts, whether intended or not, contain more than two elements. In this chapter, the adsorption properties of the simplest form of a ternary TMO – a doped binary TMO – is studied.

Three key take-away messages from the previous chapter influence the work presented in this chapter. First, the similarities between adsorption mechanisms on TM and TMOs motivates continued investigations of electronic structure relationships. However, correlations between adsorption and *d*-state properties could not be established across the entire transition metal series. A frequent observation was that electronic structure behavior differed depending on whether the TMO was an early, mid, or late transition metal. Hence, the work in this chapter is focused on only late TMOs.

The third key observation from the previous chapter was the complexity of the electronic structure through the introduction of oxygen in the lattice. In addition to the *d*-states in the TMO that remained at a similar energy level to the *d*-states in the corresponding TM, additional bonding and anti-bonding states were created through the introduction of *M*-O bonds. The complexity of these electronic structure features are addressed in this chapter.

8.1 Introduction

Accelerated materials discovery is key to the achievement of many current technological goals aimed at reducing our dependence on fossil fuels and realizing green production of chemicals.^{22,129} Metal oxides catalyze a number of chemical reactions that lie in these focus areas. These applications include

hydrogen production via water electrolysis,¹² oxygen reduction for the oxidation of fuels in solid oxide fuel cells (SOFC),¹³ conversion of sunlight into chemical energy via photocatalytic water-splitting,¹⁴ and general oxidation/reduction reactions for chemical production.^{1,2,130} The chemical property that dominates trends in the observed activity in many of these applications is the adsorption energy of various intermediate species.^{82,131–133} One strategy to easily tune the adsorption energy to obtain desirable properties is by doping or mixing an oxide with a different transition metal species.^{3,85,90}

Identification of such dopant-host pairs can be accelerated through models that relate their known chemical properties (e.g., electronegativity, atomic size) to desired chemical properties such as adsorption energies. These models already exist for the selection of metal alloy materials in a few applications,^{115,116} and their development using density functional theory (DFT) calculations has been illustrated in a number of studies.^{107,119,134} Two strategies used in these studies are highlighted. One, DFT calculations can be performed in a manner that isolates the interactions that determine the performance of alloys with respect to their pure constituents. From DFT studies, the ligand and strain effects have been identified in metals.^{108,113,135} Two, the electronic structure can be used to relate these effects to both known chemical properties and adsorption energies. For late transition metal surfaces, the adsorption energy can be correlated with the surface projected *d*-band center and width, which is then correlated to the atom's interatomic matrix element.¹¹⁴ In this Chapter, these ideas are extended to adsorption on doped oxide surfaces.

In this chapter, these two strategies are used to search for relationships between electronic and chemical properties that describe trends on doped

late transition metal oxides. The change in the adsorption energy on a specific transition metal oxide when doped into another oxide, which we call a "dopant" effect, is decomposed into a ligand and strain effect. The ligand and strain effects are then validated to be able to describe the dopant effect. Through the study of a number of electronic structure features, the center, filling, and width of the t_{2g} -band of the metal at the adsorption site best describes the trends in adsorption energy. Relationships with features of the t_{2g} -band are then used to determine that charge transfer between adjacent metal atoms is the primary mechanism of the ligand effect. The strain effect results in a correlation between the adsorption energy, strain, and properties of the t_{2g} -band that are dependent on the occupancy of the d -states. Simple correlations between known chemical properties and the magnitude of the strain and ligand effect are laid as a groundwork for future predictive models.

8.2 Methods

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP)^{124,125} with the Perdew-Burke-Ernzerhof (PBE)^{18,19} generalized gradient approximation (GGA) exchange-correlation functional. The core electrons were described by the projector-augmented wave (PAW) method.^{126,127} The Kohn-Sham orbitals were expanded with plane-waves up to a 500 eV cutoff. All k -points were represented on Monkhorst-Pack grids⁸⁷ with a $7 \times 7 \times 1$ k -point grid.

It is well known that the d -electrons of transition metal oxides contain correlation effects that are not accurately captured using standard GGA exchange correlation functionals, and the inclusion of a Hubbard U or partial exact exchange is required to capture accurate properties.^{25,27} These corrections were not included for a number of reasons. The high

computational cost of using hybrid functionals makes it infeasible considering the number of calculations performed in this work. The inclusion of the Hubbard U was neglected because this study is focused on adsorption energy trends between different systems and their relationship with the electronic structure. Previous work have shown that neither of these properties change with respect to the Hubbard U . Work from Chapter 5 on adsorption energies on transition metal oxides show that the inclusion of the Hubbard U does not change trends between different systems.¹³⁶ In addition, recent work on TiO₂ doped with transition metals found similar electronic structure correlations with and without the addition of the Hubbard U .¹³⁷

The band center, width, and fractional filling of different surface atom projected electronic structure features were calculated. The formulas used are below.

$$E_l = \frac{\int \rho E dE}{\int \rho dE} \quad (8.1)$$

$$W_l^2 = \frac{\int \rho (E - E_l)^2 dE}{\int \rho dE} \quad (8.2)$$

$$f_l = \frac{\int_{-\infty}^{E_f} \rho dE}{\int_{-\infty}^{\infty} \rho dE} \quad (8.3)$$

Given states l , the band center (E_l), was computed as the first moment of the projected density of states about the Fermi level (E_f), shown in Equation (8.1). The band width (W_l) is computed as the square-root of the second moment of projected density of states about the band center, shown in Equation (8.2). The fractional filling (f_l) is taken as the integral over states up to the Fermi level divided by the integral over all states, shown in Equation (8.3).

When studying doped oxides, many theoretical studies examine how a specific material's property is changed by doping in another metal.^{138–140} Instead, in this chapter the problem is approached from a different angle by asking the question, "How are the chemical properties of a specific atom changed when it is doped into another system?" The chemical property analyzed in this study is the dissociative adsorption energy of atomic oxygen. Given dopant atom M^D and host atom M^H , the adsorption energy on $M^H\text{O}_x$ doped with M^D ($M^D\text{-}M^H\text{O}_x$), where M^D is the adsorption site, is hypothesized to be able to be described by the adsorption energy of M^D in its native oxide $M^D\text{O}_x$ and the perturbations to its electronic structure caused by placing it inside the oxide of the host, $M^H\text{O}_x$. These perturbations are deconvoluted into a strain and ligand effect, which make up what will be called in this chapter a "dopant" effect. This methodology is shown in Figure 8.1.

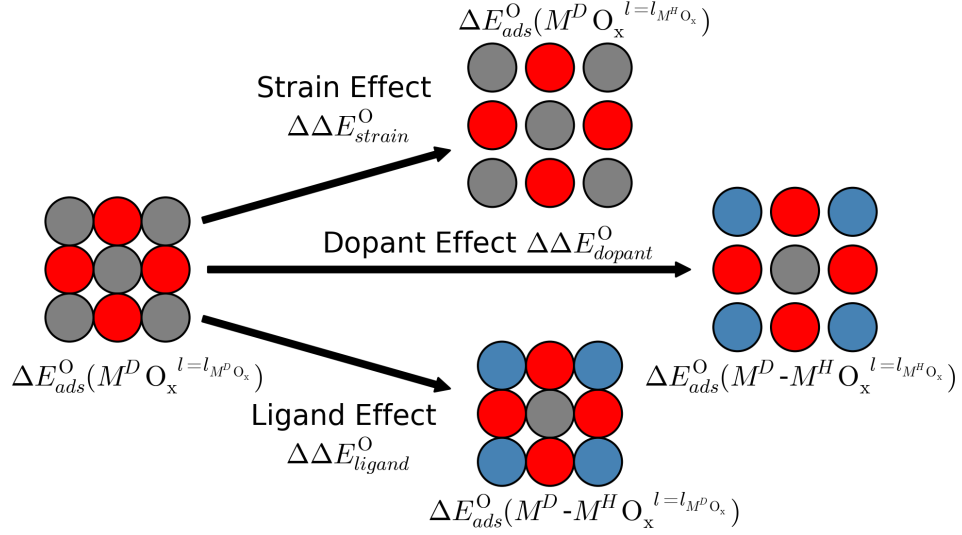


Figure 8.1: Illustrates the components, the strain and ligand effect, that produce the change in the adsorption energy upon doping cation M^D (gray circles) from its native oxide into the oxide of cation M^H (blue circles), which is called the "dopant" effect. Given a single M^D - M^H dopant-host pair, adsorption energies on all four systems shown were calculated. With six transition metals studied and not double counting multiple adsorption energies on $M^D O_2$ in systems with common dopants, this totaled to 96 adsorption energies.

The calculated quantities required to address this hypothesis are as follows. Given a dopant-host system M^D - $M^H O_x$ with dopant-host pair M^D - M^H , the ligand, strain, and dopant effects on the adsorption energy of atomic oxygen are defined as as differences in adsorption energies shown in the Equations (8.4), (8.5), (8.6) below, respectively.

$$\Delta\Delta E_{ligand}^O = \Delta E_{ads}^O(M^D-M^H O_x^{l=l_{M^D} O_x}) - \Delta E_{ads}^O(M^D O_x^{l=l_{M^D} O_x}) \quad (8.4)$$

$$\Delta\Delta E_{strain}^O = \Delta E_{ads}^O(M^D O_x^{l=l_{M^H} O_x}) - \Delta E_{ads}^O(M^D O_x^{l=l_{M^D} O_x}) \quad (8.5)$$

$$\Delta\Delta E_{dopant}^O = \Delta E_{ads}^O(M^D-M^H O_x^{l=l_{M^H} O_x}) - \Delta E_{ads}^O(M^D O_x^{l=l_{M^D} O_x}) \quad (8.6)$$

$\Delta E_{ads}^O(M^D O_x^{l=l_{M^D O_x}})$, the reference for the described perturbations, is the adsorption energy of O onto oxide $M^D O_x$ with its lattice parameters, l , equal to those of its equilibrium structure, $l_{M^D O_x}$. $\Delta E_{ads}^O(M^D-M^H O_x^{l=l_{M^D O_x}})$ is the adsorption energy of O onto the same $M^D O_x$ structure with every metal cation except the metal cation at the adsorption site is replaced with M^H . $\Delta E_{ads}^O(M^D O_x^{l=l_{M^H O_x}})$ is the adsorption energy of O onto a structure of $M^D O_x$ except the lattice parameters, l , are those of the relaxed $M^H O_x$ structure ($l_{M^H O_x}$). Finally, $\Delta E_{ads}^O(M^D-M^H O_x^{l=l_{M^H O_x}})$ is the adsorption energy of O onto an equilibrium $M^H O_x$ surface with the adsorption site doped with a M^D metal atom.

The set of doped oxides used in this study is all the possible dopant-host, M^D-M^H , pairs of six late 4d and 5d transition metals (Ru, Rh, Pd, Os, Ir, Pt) in the +4 oxidation state within the rutile crystal structure. This comes to a total of 30 unique M^D-M^H pairs. For each dopant-host pair, four separate adsorption energy calculations were required to evaluate the ligand, strain, and dopant effect. Not double counting M^D-M^H pairs that share a common M^D and therefore the same $\Delta E_{ads}^O(M^D O_x^{l=l_{M^D O_x}})$ calculation, this totals to 96 adsorption energies. All adsorption energies were calculated on the (110) surface in four layer slabs with the top two layers allowed to relax. The adsorption site was the *5cus* site with bridge oxygen sites occupied and a *5cus* coverage of 0.5 ML, which equates to a 2×1 surface unit cell.

This study focuses on this set of systems for a number of reasons. One, results in Chapter 7 found no universal, surface projected *d* or *p*-band property which gave strong correlations with adsorption energies for the entire row of 3d transition metal monoxides.¹⁴¹ Features of the *d*-band that interacted with the adsorbate *p*-band was determined by whether the cation was an early, mid, or late transition metal. Two, an extensive review on catalysis by doped

oxides has identified the category of systems doped with same-valence dopants (SVDs) or flexible-valence dopants (FVDs) that lacked simple rules describing their behavior.¹⁴² In contrast, low-valence dopants (LVDs) and high-valence (HVDs) can be qualitatively understood by simple electron counting rules.¹⁴³ This study is focused on dopant-host pairs that constitute SVDs and FVDs, but the principles from this work may also be used for analysis of LVDs and HVDs. Third, all systems modeled were in the rutile phase, thereby simplifying the interpretation by eliminating changes in the adsorption energy caused by a major changes in the crystal structure. Chapter 9 will explore how crystal structure modifications change adsorption.

8.3 Results and Discussion

The organization of the results and discussion in this chapter is as follows. In Section 8.3.1, the decomposition of the dopant effect into separate ligand and strain effects is validated. This allows the investigation of relationships between the adsorption energy and the electronic structure within the context of the ligand and strain effects separately in Sections 8.3.3 and 8.3.4, respectively. Prior to this, a number of electronic structure correlations with all adsorption energies in this study are investigated to help pinpoint the key features this analysis should be focused on. This is done in Section 8.3.2 before analysis of the ligand and strain effect.

8.3.1 Validation of Strain and the Ligand Effect

As detailed in the methods, the ligand, strain, and dopant effects are defined as the change in the adsorption energy of M^D in the equilibrium structure of $M^D\text{O}_2$ caused by perturbations of changing its neighboring metal cations (ligand), lattice parameters (strain), and both (dopant),

respectively. When studying the dopant effect by directly doping cation M^D into the lattice of $M^H\text{O}_2$, it is likely that both ligand and strain play separate roles in explaining the adsorption energy. It would be convenient if these effects could be studied separately. Their relationships with chemical and electronic properties could then be isolated.

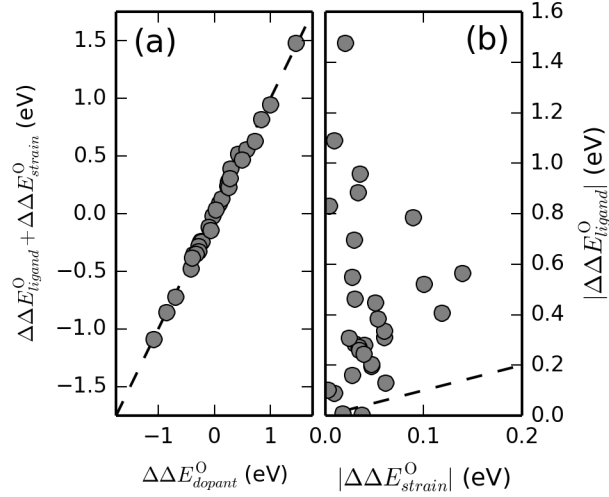


Figure 8.2: Validation that the strain and ligand effect can accurately describe the dopant effect (a) and the relative magnitudes of both effects (b) for dopant-host combinations that included all permutations in the set of RuO_2 , RhO_2 , PdO_2 , OsO_2 , IrO_2 , and PtO_2 .

Figure 8.2 (a) shows that the simple addition of the ligand and strain effect results in excellent agreement with the dopant effect for all 30 dopant-host pairs considered in this study. This suggests that isolated analysis of both the ligand and strain effect will produce a more complete understanding of the dopant effect. The absolute value of the ligand effect is up to an order of magnitude higher than the strain effect, shown in Figure 8.2 (b). This was a surprising result. Because all metal cations form stable +4 oxidation states and metal cations are not typically adjacent in oxide structures, significant interactions were not expected via charge transfer, which is present in LVD and HVD

systems,¹⁴⁰ nor direct orbital overlap of metal orbitals, which characterizes the ligand effect in metal systems.¹¹³ The next step in this analysis is to understand these effects by looking at correlations with the electronic structure.

8.3.2 Identification of Electronic Structure Descriptors

The electronic structure contains all of the information required to relate the structure and composition of the system to its chemical properties and is readily available from DFT calculations.⁷⁶ The difficulty lies in extracting the most important features of the electronic structure. The *d*-band model, which relates easily calculated properties such as its center and width to chemical properties, has had large success in metal systems due in large part to the simplicity of both their atomic and electronic structure. For example in metal systems, the five *d*-orbitals are degenerate in energy and form a single band, though recent work studying Pt overlayers found that the center of the sum of d_{xz} , d_{yz} , and d_{z^2} states gave better correlations with adsorption than the entire *d*-band.¹⁴⁴

In oxides, the crystal field theory model describes how the degeneracy of the *d*-states is lifted into the t_{2g} and e_g -states when the transition metal is octahedrally coordinated with six other oxygen molecules.¹⁴⁵ The e_g ligands point toward the six oxygen cations and therefore form low and high energy bonding and anti-bonding states, while the t_{2g} -states are non-bonding and energetically lie between the low and high energy e_g -states. In addition to the metal cation's *d*-states, the oxygen *p*-states also participate in bonding in oxides through interactions with the *d*-states of metals. Figure 9.4 illustrates these characteristics with a sample atom projected density of states (DOS) of the metal cation at the adsorption site and the four surface and one subsurface oxygen atoms bonded to this adsorption site.

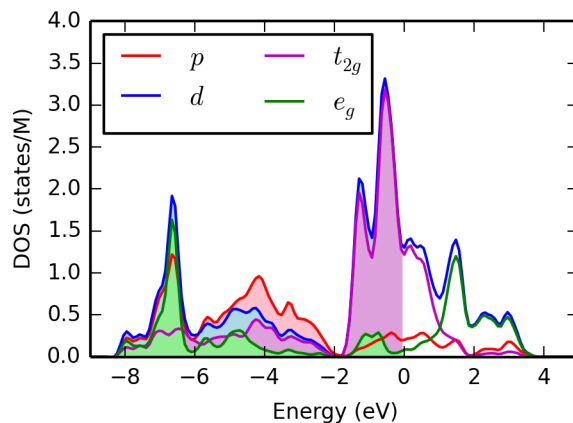


Figure 8.3: Sample atom-projected, phase-separated density states of RuO_2 . Includes the d (blue), e_g (purple), and t_{2g} -states (green) of the cation at the $5cus$ adsorption site and p -states (red) of the four surrounding surface and one subsurface coordinated oxygen anion. Shaded regions show occupied states. All densities are normalized on a per atom basis.

The goal of this chapter is to correlate features of these states to adsorption energies for the systems tested. Previous work has already shown correlations of chemical properties of transition metal oxides with the center of the d -states,^{96,137} center of bulk oxygen p -states,¹²¹ occupancy of the e_g -states,^{83,84} and occupancy of the t_{2g} -states.⁸⁴ Figure 8.4 shows correlations between the O adsorption energy of all adsorption energies and the center of the atom projected d , e_g , and t_{2g} -band of adsorption site and p -band of the surface oxygen atoms. Many correlations exist between the electronic structure features and adsorption for systems with the same element at the adsorption site. The feature that showed the best universal correlations with all adsorption energies was the t_{2g} -band center. The correlation is dependent on whether the adsorption site is a row 4 or row 5 transition metal. Inspection of the density states reveal that for all of materials tested in this chapter, the t_{2g} states lie near the Fermi level. This observation is consistent with strong correlations between surface states near the Fermi level and the

adsorption energy found for transition metal carbides and doped TiO_2 .^{137,146} Now that it has been identified that features of the t_{2g} -states could be a strong descriptor of adsorption, this information is used to elucidate the underlying physics of the ligand and strain effect.

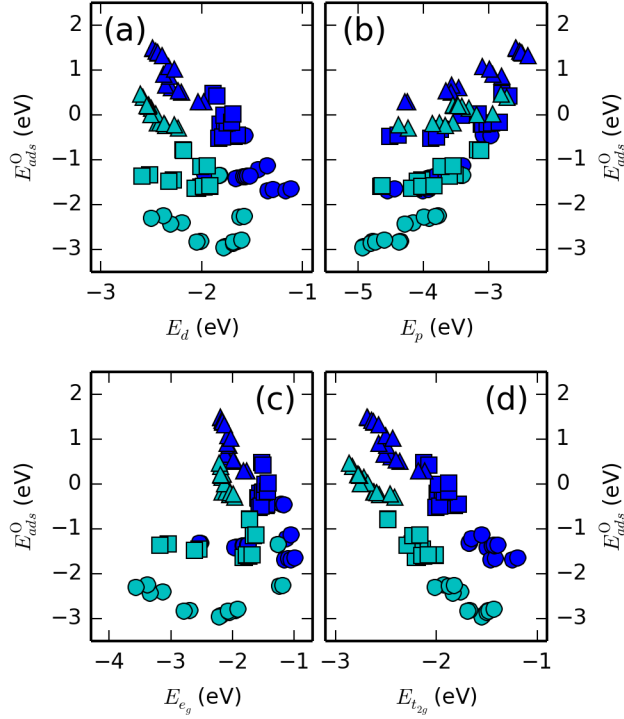


Figure 8.4: Correlations of the center of the (a) metal d -band, (b) oxygen p -band, (c) metal e_g -band, and (d) metal t_{2g} -band with all calculated adsorption energies of atomic oxygen in this study. All properties of the electronic structure were taken from the bare surface. Blue and cyan markers show systems where M^D is a row 5 and 6 metal, respectively. Circle, square, and triangle markers show systems where M^D is a column 8, 9, and 10 metal, respectively.

8.3.3 Relationships Between the Ligand Effect and the Electronic Structure

In the Section 8.3.2, analysis of correlations between electronic features and adsorption energies of all systems showed a strong correlation with the center of the t_{2g} -band. The objective now is to use this information to uncover

the underlying physics of the ligand effect. Figure 8.5 shows that the ligand effect ($\Delta\Delta E_{ligand}^O$) shows a strong correlation with changes in the center of the t_{2g} -band ($\Delta E_{t_{2g}}$). Perturbing the dopant M^D by replacing its $M^D O_2$ atomic environment with M^H cations results in shifts to the t_{2g} -band center and an inverse relationship to its adsorption energy. This relationship is reminiscent of the d -band model in metals and also observed in previous studies with correlations of the entire d -band,^{96,137} though in this case the t_{2g} -band gave a stronger correlation than the d -band. One explanation for this correlation is that the energies of t_{2g} -states determines the energies and fillings of the bonding and anti-bonding states of the adsorbed O atom. If the t_{2g} -states have a lower (higher) center, then the adsorbate anti-bonding states will be less (more) occupied, resulting in stronger (weaker) adsorption.⁸⁴

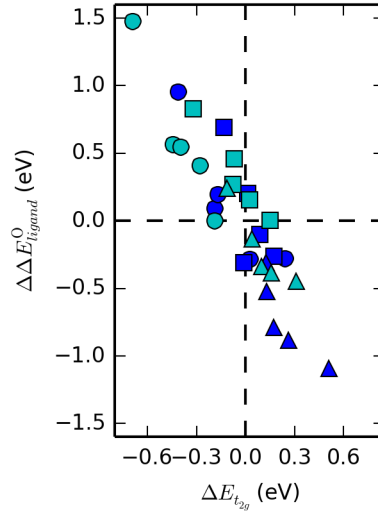


Figure 8.5: Relationship between the ligand effect ($\Delta\Delta E_{ligand}^O$) in system M^D - $M^H O_2$ and the corresponding difference in the center of the t_{2g} -band ($E_{t_{2g}}$) between the system $M^D O_2$ and M^D - $M^H O_2$ with the lattice constant of $M^D O_2$. Blue and cyan markers show systems where M^D is a row 5 and 6 metal, respectively. Circle, square, and triangle markers show systems where M^D is a column 8, 9, and 10 metal, respectively.

While these observations relate the ligand effect to known relationships between electronic and chemical properties, it is still unclear the exact mechanism of the ligand effect. In metal systems, the ligand effect can be understood by changes in the d -band center caused by overlap between atomic orbitals of neighboring atoms that resulted in changes to the shape of the d -band but conservation of total states.^{113,147} Figure 8.6 (a) hints that a similar mechanism might explain ligand effect in oxides by showing linear correlations between the t_{2g} -band width and center, which is observed for the ligand effect in metals. Also similar to the ligand effect in metals is that metal cations in the same column lie on the same correlation.¹¹⁴ However, unique to the ligand effect on oxides is that the filling of the t_{2g} -band is not constant. Figure 8.6 (b) demonstrates that the changes in the center of the t_{2g} -band are caused by changes in the number of occupied states. Interestingly, increases in the number states, which are expected to result in a more noble-like character of the metal cation, results in positive shifts in the t_{2g} -band center, which describes less noble-like character and hence a stronger adsorption energy (Figure 8.5). Upon analyzing relationships between the filling of the t_{2g} and e_g -band, it was concluded that this change did not come from redistribution of states within the d -band. The most likely source was charge transfer with neighboring atoms.

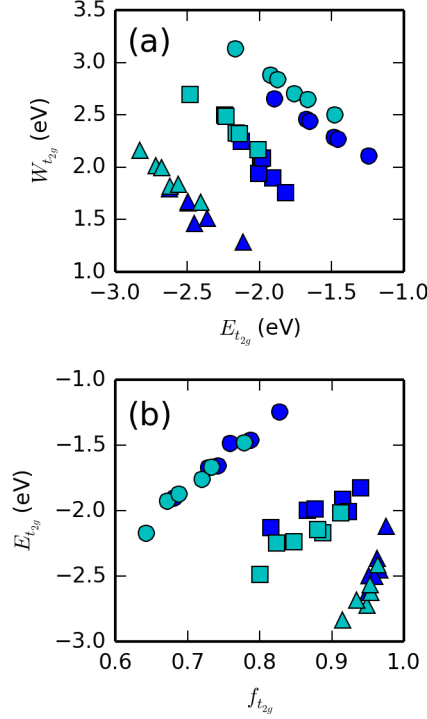


Figure 8.6: Relationship between the (a) M^D t_{2g} -band center ($E_{t_{2g}}$) and width ($W_{t_{2g}}$) and the (b) M^D t_{2g} fractional filling ($f_{t_{2g}}$) and center ($E_{t_{2g}}$) of systems where M^D is either in its native lattice $M^D\text{O}_2$ or is under the ligand effect, $M^D\text{-}M^H\text{O}_2^{l=l_{M^D}\text{O}_2}$. Blue and cyan markers show systems where M^D is a row 5 and 6 metal, respectively. Circle, square, and triangle markers show systems where M^D is a column 8, 9, and 10 metal, respectively.

To investigate whether the addition or loss of electrons on the metal cation produced by the ligand effect comes from charge transfer with neighboring oxygen cations, ligand effect induced changes of the fractional filling of the d -states was correlated with that of the oxygen p -states (Figure 8.7 (a)). Surprisingly, an increase/decrease in the fractional filling of the d -states caused by the ligand effect results in a corresponding increase/decrease in the fractional filling of the p -states of neighboring oxygen cations. This means that oxygen cations only mediate the charge transfer and are not the source of it.

One hypothesis is that the source of the charge transfer to M^D under the ligand effect must come from the host M^H cations. To test this hypothesis, changes in the fractional filling of the oxygen p -states (Δf_p) under the ligand effect, where the dopant-host pair is M^D - M^H , are related to changes in the fractional filling of the d -band of the host metal cation M^H when it is doped into the $M^D\text{O}_2$ system (Δf_d^{host}). If this hypothesis is correct, an inverse relationship between Δf_p and Δf_d^{host} should be observed, implying charge from M^H was transferred to the oxygen in an M^D environment. Figure 8.7 (b) shows that this is case, where the slope of the relationship is close to $\Delta f_p = -\Delta f_d^{host}$. This is clear evidence that changes in the charge on the M^D caused by the ligand effect come from electrons transferred from M^H cations. Interestingly, charge transfer is still evident even when the formal oxidation state of all these species is expected to be +4.

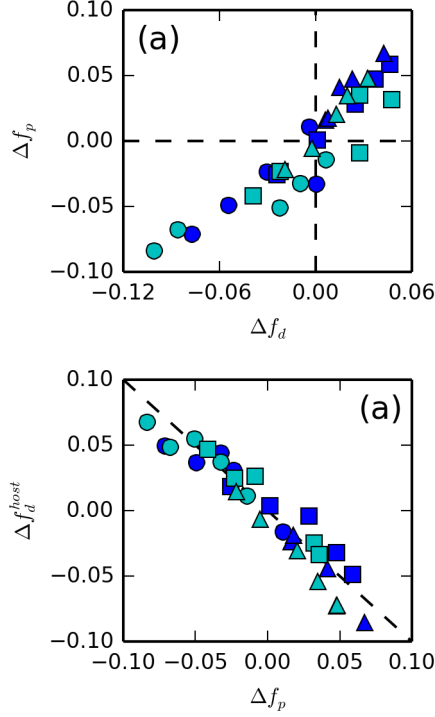


Figure 8.7: (a) Relationship between the change on the M^D d -band filling (Δf_d) and bonded oxygen p -band filling (Δf_p) caused by the ligand effect. Black dashed lines show the $x=0$ and $y=0$ axis. (b) Relationship between the change in the bonded oxygen p -band filling (Δf_p) caused by the ligand effect in system M^D - M^H O₂ and the change in the M^H d -band filling (Δf_d^{host}) caused by the ligand effect in system M^H - M^D O₂. Black dashed line in (b) shows the $\Delta f_d^{host} = -\Delta f_p$ line. Blue and cyan markers show systems where M^D is a row 5 and 6 metal, respectively. Circle, square, and triangle markers show systems where M^D is a column 8, 9, and 10 metal, respectively.

Having understood the nature of the ligand effect, the next goal is to understand which properties of the dopant-host pair determines the direction and magnitude of the charge transfer. Differences in TM electronegativities were first suspected to correlate with the ligand effect, but this was not the case. Going back to calculated electronic properties, and it was found that the difference between the widths of dopant and host TM t_{2g} -states correlates the best with the ligand effect (Figure 8.8 (a)). Recent work from the Kitchin group found that the d -band width of metal cations in perovskites has a linear

correlation with the effective orbital radius raised to the 3/2 power ($r_d^{3/2}$).¹²² The present results suggest that differences in $r_d^{3/2}$ of the dopant-host pair should also correlate with the ligand effect. Figure 8.8 (b) shows that this is the case. Though the correlation of the ligand effect with the differences in effective orbital radius is weaker than the correlation with the difference in the calculated t_{2g} -band width, $r_d^{3/2}$ is a known chemical property that can be looked up from solid state tables.¹⁴⁸ This observation can be the foundation of future work that creates predictive models of adsorption energies on oxides.

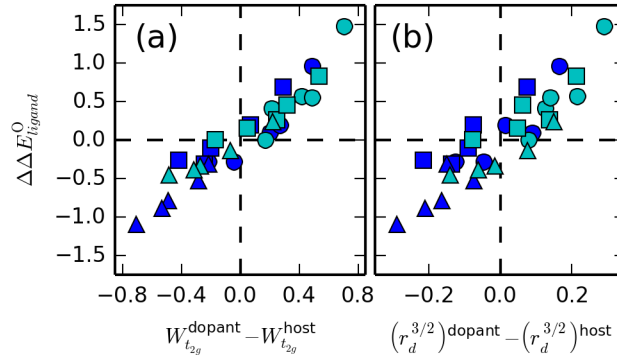


Figure 8.8: Relationship between the ligand effect ($\Delta\Delta E_{ligand}^O$) in the dopant-host system $M^D-M^H\text{O}_2$ and the difference in (a) the t_{2g} -band width ($W_{t_{2g}}$) and (b) the tabulated effective orbital radius to the 3/2 power ($r_d^{3/2}$) of dopant M^D and host M^H . Black dashed line in both (a) and (b) show the $x=0$ and $y=0$ axis. Blue and cyan markers show systems where M^D is a row 5 and 6 metal, respectively. Circle, square, and triangle markers show systems where M^D is a column 8, 9, and 10 metal, respectively.

Correlations shown in Figures 8.5 – 8.8 have a number of implications of the underlying physics dominating the ligand effect. Figure 8.8 shows that a dopant cation M^D with a larger t_{2g} -band width and r_d effective orbital radius than its host cation M^H would experience a more endothermic adsorption with respect to $M^D\text{O}_2$. According to Figure 8.5 and 8.6, the t_{2g} -band center would shift down to lower energies, in turn implying that charge was transferred away from the M^D (Figure 8.6 (b)).

In short, a M^D dopant with a larger/smaller atomic radius than its M^H host loses/gains electrons from M^H . The nature of this interaction is hypothesized below. If a M^D is placed into an environment where its r_d is larger/smaller than the M^H 's, there will be an increase/decrease in the overlap between the M^D orbital and oxygen p orbital, resulting in the creation of hybridized states. Due to Pauli Repulsion, these states will be less/more energetically stable than hybridized states by replaced M^H with a smaller/larger r_d term. If an increase in overlap creates less stable states, charge transfer towards the M^H host cations will ensue to lower the energy of these states. Likewise, if a decrease in the overlap results in more stable states, these states will be filled with electrons from the M^H host cations. This charge transfer creates shifts in the center of the t_{2g} -band, which in turn leads to changes in the adsorption energy on the M^D cation.

8.3.4 Relationships Between Strain and the Electronic Structure

Having understood the nature of the ligand effect and established correlations between the adsorption energy and both the chemical and electronic properties, the next objective is understanding the strain effect, which is an order of magnitude smaller than the ligand effect (Figure 8.2 (b)). This result is consistent with those found by a previous study from the Kitchen group, which determined that the effect of strain is much smaller compared to changes in d -band filling.⁹⁶ However, in that study correlations between the adsorption energy and d -band center of strained $3d$ perovskites were dominated by the number of d -electrons, and the subtle relationship between the electronic structure and the adsorption energy in the context of strain remained elusive.

Figure 8.9 shows that the effect of strain on the change in the adsorption energy is unique to the metal cation undergoing strain. This observation is consistent with those found in previous results on oxides⁹⁶ and metals.¹²⁸ Interestingly, only adsorption on noble metal cations Pd and Pt becomes more endothermic with the application of compressive strain, while the opposite is true for the rest of the metal cations. This behavior is in contrast to metals, where compressive strain generally results in endothermic adsorption energies of all late transition metals.¹⁰⁸

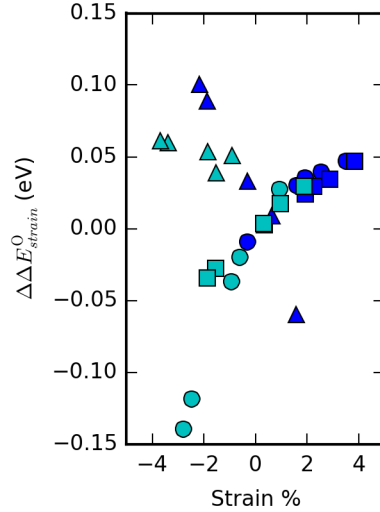


Figure 8.9: Relationship between the relative strain in the direction parallel to the surface and the change in the adsorption caused by the strain ($\Delta\Delta E_{strain}^O$). Blue and cyan markers show systems where M^D is a row 5 and 6 metal, respectively. Circle, square, and triangle markers show systems where M^D is a column 8, 9, and 10 metal, respectively.

To understand these correlations, relationships between strain and the electronic structure were examined. Because the d -band width is related to the amount of overlap between the interatomic matrix elements of neighboring atoms, compressive/tensile strain should result in an increase/decrease in the d -band width. This observation has already been observed for bulk perovskites.¹²² Figure 8.10 (a) shows this to be the case for

the t_{2g} -band as well in rutile dioxides. Furthermore, a positive correlation is also observed between strain and the t_{2g} -band center. The inverse and proportional relationship of strain with changes in the t_{2g} -band center and width, respectively, also imply that in the context of strain, the t_{2g} -band center and width have an inverse relationship. In contrast to the ligand effect, which is also mediated by differences in the overlap of atomic orbitals, no charge transfer was found. This is attributed to the symmetry of the strain effect, where the strain induced change in the overlap of atomic orbitals is experienced equally among all metal cations, while the ligand effect produces an asymmetric change that results in charge transfer. This observation suggests in response to strain-induced changes in the t_{2g} -band width, the t_{2g} -band center must shift to conserve states, which is consistent with models established on transition metals.^{108,128}

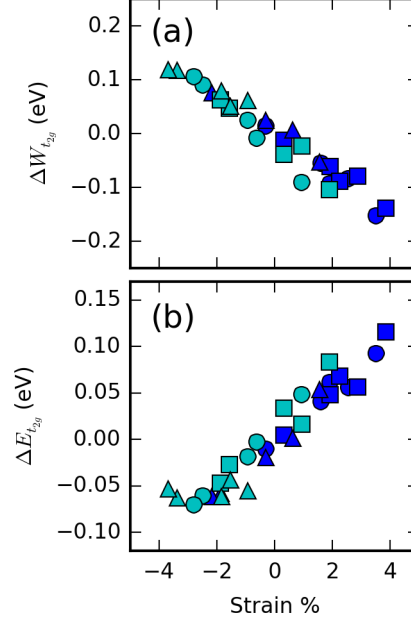


Figure 8.10: Relationship between the relative strain in the direction parallel to the surface and the change in the (a) t_{2g} -band width ($\Delta W_{t_{2g}}$) and (b) t_{2g} -band center ($\Delta E_{t_{2g}}$). Blue and cyan markers show systems where M^D is a row 5 and 6 metal, respectively. Circle, square, and triangle markers show systems where M^D is a column 8, 9, and 10 metal, respectively.

These correlations between strain and the features of the t_{2g} -states imply one can estimate changes to the electronic structure based on the strain, and these correlations are independent of the metal cation studied. However, Figure 8.9 and 8.10 suggests that correlations between the electronic structure and adsorption energy *are not* independent of the metal cation studied. This implication is shown to be true in Figure 8.11 (a). Note that due to the linear correlations between strain and the t_{2g} -band center shown in Figure 8.10 (b), the relationships between the t_{2g} -band center and the strain effect largely mirror relationships between the amount of strain itself and the strain effect shown in Figure 8.9. We therefore conclude that the element specific correlation between strain and the adsorption energy is due to each element's unique relationship between the electronic structure and adsorption energy. This is not observed for metal systems, where it is found that despite the relationship between strain and the electronic structure, for both early and late transition metals the correlations between the electronic structure and the adsorption energy were the same.^{108,128}

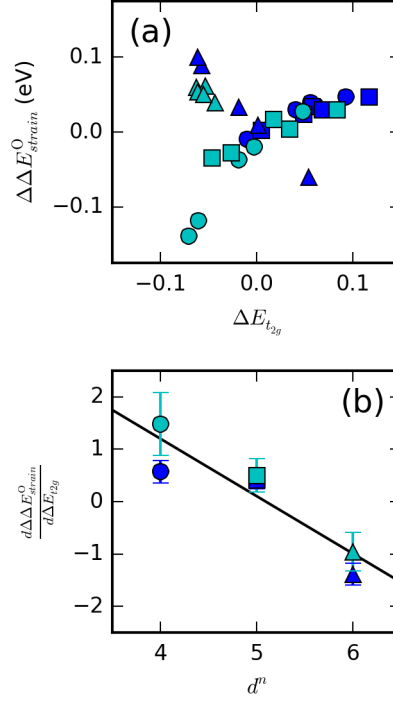


Figure 8.11: (a) Relationship between the change in the t_{2g} -band center ($\Delta E_{t_{2g}}$) due to strain and the change in the adsorption energy due to strain ($\Delta\Delta E_{strain}^O$) (b) Relationship between the idealized occupancy of the d -states of M^D and the fitted slope of the relationship between shown in (a) for different M^D dopants. Errorbars in (b) are the 95% confidence intervals of the fit in (a). Blue and cyan markers show systems where M^D is a row 5 and 6 metal, respectively. Circle, square, and triangle markers show systems where M^D is a column 8, 9, and 10 metal, respectively.

Following the ability to predict changes in the electronic structure produced by strain (Figure 8.10), the final goal is to obtain some insight into the nature for the element specific relationships between the t_{2g} -band center and the adsorption energy found in Figure (8.11). The slope of this relationship ($\frac{d\Delta\Delta E_{strain}^O}{d\Delta E_{t_{2g}}}$) was inversely proportional to the idealized filling of the d -band. Metal cations with an idealized d -band that was over half filled (Pt and Pd) obey the model that is observed in Figure 8.4 (d) and 8.5 for the ligand effect, where a downshift in the t_{2g} -band produces more endothermic adsorption energies. However, metal cations with the d -band at

half filling or lower show the opposite behavior. This observation necessitates the deconvolution of the dopant effect into the ligand and strain effect, since their effects on reactivity do not follow the same electronic structure-adsorption relationships. In fact, the larger magnitude of the ligand effect (Figure 8.2 (b)) probably dominates the observed correlation between the t_{2g} -band center and the adsorption energy found for all adsorption energies in Figure 8.4 (d).

The underlying physics that describe the relationship between strain and the adsorption energies is elusive but warrants some discussion. The key difference between the ligand and strain effect is that ligand-induced changes to the electronic structure arise from charge transfer and strain-induced changes to the electronic structure arise from differences in the overlap of atomic orbitals, which altered the widths of many features of the electronic structure. Changes to the shape of both the e_g and t_{2g} -band have complex interactions with the adsorption energy. For example, work in Chapter 7 showed that low energy, bonding orbitals of the e_g -states are responsible for the stabilization of surface-adsorbate bonds, while high energy, anti-bonding e_g -states serve to destabilize the bond.¹⁴¹ While systematic changes to the width of the e_g -band caused by strain were found, no simple correlations between the width, center, and filling between the e_g -band and the strain effect were discovered. However, changes in the e_g -band width and center due to strain probably causes shifts in energy to both the e_g bonding and anti-bonding states, which was difficult to quantify. One possible strategy would be to take into account the shape of the t_{2g} and/or e_g -band. This has been done on transition metals using the band width¹⁴⁹ and the Newns-Anderson model.¹⁵⁰ However, these interactions are most likely somehow manifest in correlations of the strain effect with the center of the

t_{2g} -band – which is more easily characterized than the e_g band – and the relationship of $\frac{d\Delta E_{strain}^O}{d\Delta E_{t_{2g}}}$ with the idealized d^n filling shown in Figure 8.11.

8.4 Conclusions

In summary, DFT calculations were performed to understand the underlying physics that dominate the trends in the dissociative adsorption energy of oxygen on doped transition metal oxides. Adsorption energies on doped rutiles M^D - M^H O₂ were expressed as a combination of adsorption on the pure oxide of the dopant M^D O₂ and perturbations to this adsorption energy caused by changing its neighboring metal cations (ligand effect) and lattice constant (strain effect).

After validating that the ligand and strain effect can describe the dopant effect, an understanding of the underlying physics of both the ligand and strain effect on the adsorption energy was developed by relating both of these effects to changes in the electronic structure. The ligand effect is expressed as changes to the t_{2g} -band center that mirror the d -band model on metal systems. Changes to the t_{2g} -band center from the ligand effect are caused by charge transfer between the dopant and host metal cation, mediated by the lattice oxygen. The magnitude and direction of the ligand effect was correlated to differences in the d -orbital radii of dopant and host metal cation. The physical nature of this mechanism was then discussed in terms of the orbital overlap of d -orbitals.

Strain systematically changes the widths of many features of the electronic density of states, but in contrast to the ligand effect, strain induced changes to the adsorption energy and t_{2g} -band center do not follow the same electronic structure correlation that describes the ligand effect or those found in metal systems. In spite of the elusive underlying physical mechanisms that explain

the strain effect, the idealized filling of the d -band can describe the slopes of correlations between changes in the t_{2g} -band center and the strain effect. This work introduces a number of novel techniques and relationships that elucidate the underlying physics of adsorption on doped oxides and establishes a ground work for possible predictive models for the reactivity of doped oxides.

9 Surface Chemical and Electronic Properties of Polymorph TMOs

The previous chapter highlighted the dominance of composition induced changes to the adsorption energy over structure induced changes. However, structural differences between TMOs in the previous chapter was limited to strain. This chapter explores the potential of modifications to the crystal structure for tuning adsorption on TMOs. Analysis in this chapter was performed within the context of the t_{2g} and e_g -band introduced in the previous chapter. This chapter also adds an additional calculated chemical property: the bulk oxygen vacancy formation energy. While arguably not as relevant towards TMO catalysis as a surface adsorption energy, the ramifications of the oxygen vacancy formation energy towards TMO stability warrants their investigation. In addition, oxygen vacancy formation and adsorption – both of which involve charge transfer – have similar chemistries.

9.1 Introduction

The discovery of new materials with tailored chemical properties is vital for advancing key technologies related to catalysis and energy conversion.^{22,129} Transition metal oxides (TMOs) catalyze a number of these key technologies, including water electrolysis, fuel cells, and photocatalysis.^{151–153} Compared to modifying the composition of TMOs, the search for novel structures for catalytic applications is relatively unexplored. The impact of the crystal structure on catalytic activity is often difficult to pinpoint experimentally. For oxygen evolution, slight changes to bond lengths/angles of amorphous materials result in orders of magnitude differences in activity, but these distortions are accompanied by significant

changes in the oxidation state and oxygen vacancy concentration.^{154–156} For example, a recent study found that the symmetric coordination of oxygen around the *B* ions in a mixed Pt doped BaCeO₃ perovskite was key to high water-gas shift (WGS) activity, and oxygen vacancy induced distortions to this symmetry lowered WGS activity.¹⁵⁷ Elucidation of these structure-function relationships would allow for the targeted synthesis of materials with optimized crystal structures.

Polymorph engineering is one potential route to structurally tune the activity of materials. Experimental studies have observed that some metastable polymorphs can lead to significant improvements in catalytic reactions. Multiple polymorphs of Al₂O₃ that are stable in reactive conditions have been observed to display different support effects.^{10,158} Anatase TiO₂ has been observed to be more photocatalytically active than rutile TiO₂.¹⁵⁹ The structural sensitivity towards formaldehyde and water oxidation has been observed in a number of studies including manganese and cobalt oxide polymorphs.^{155,160–163}

Traditionally, variation of temperature and/or pressure during synthesis can lead to crystallization of different polymorphic structures.^{164–166} However, new strategies have proven to be effective at realizing metastable phases. Thin films of metastable polymorphs can be stabilized epitaxially if grown on an appropriate substrate.^{167,168} It has been shown that thin films are stable and active towards photocatalysis and oxygen reduction.^{169–172} Changing the composition of materials has also been shown to be effective at producing metastable phases, especially when the constituent materials have different ground state structures.^{173–175} On the nanoscale, the increase in the surface to bulk ratio can stabilize certain metastable phases if surface energies of metastable phases are preferred over stable ones.¹⁷⁶

Given the large number of potential structural polymorphs that are possible, experimental synthesis would be aided by *a priori* information on what polymorphs are possible and desirable to synthesize. Simple comparisons of calculated free energies using density functional theory (DFT) combined with automatic crystal structure generation can build large databases of relative stabilities that quickly direct what might be possible for synthesis.^{177–179} Recent DFT studies have also evaluated electronic and physical properties of potential polymorphs as well.^{180–183} While a few studies have evaluated surface activity of existing polymorphs,^{184,185} no studies have evaluated chemical properties of *potential undiscovered* polymorphs.

This chapter investigates the reactivity and stability of four potential oxide polymorphs (anatase, brookite, columbite, pyrite) of MO_2 ($M=\text{Ru, Rh, Pt, Ir}$) transition metal oxides (TMOs), which all crystallize in a rutile-like structure at typical synthesis and reactive conditions. The similar coordination and local geometry of both cations and anions in all structures lead to the hypothesis that strain alone could describe trends in chemical properties of metastable polymorphs. Results presented in this chapter suggest this is not the case. In addition, polymorphic structures provide more tunable reactivity and increased stability with respect to strained rutile structures. The prediction that columbite IrO_2 will be a better oxygen evolution catalyst than rutile IrO_2 underscores the potential activity benefits of polymorphic structure. The origin of the unique reactivity of polymorphic structures is unearthed through analysis of the electronic structure. In contrast to simple strain, distortions to the octahedral symmetry of the metal cation in polymorphic structures lead to significant changes in both the shape of the t_{2g} -band and adsorption energy.

9.2 Computational Methods

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP)^{124,125} with the Perdew-Burke-Ernzerhof (PBE)^{18,19} generalized gradient approximation (GGA) exchange-correlation functional. The core electrons were described by the projector-augmented wave (PAW) method.^{126,127} The Kohn-Sham orbitals were expanded with plane-waves up to a 500 eV cutoff. All k -points were represented on Monkhorst-Pack grids.⁸⁷

The two primary chemical properties calculated in this study are oxygen adsorption and vacancy formation energies. Using DFT computed total energy values, the formulas for both quantities are shown below.

$$\Delta E_{ads}^O = E_{slab,O} - E_{slab} - \frac{E_{O_2}}{2} \quad (9.1)$$

$$\Delta E_{vac}^O = E_{bulk,vac} + \frac{E_{O_2}}{2} - E_{bulk,stoic} \quad (9.2)$$

$E_{slab,O}$ and E_{slab} are the total energies of an oxide slab with and without an adsorbed oxygen atom, respectively. $E_{bulk,stoic}$ and $E_{bulk,vac}$ are the total energies a bulk oxide with and without an oxygen vacancy. All vacancy formation energies were calculated at a 6.25% vacancy concentration. Free energies of adsorption energies of OER intermediates were calculated using the atomistic thermodynamic framework and zero-point corrections employed in Chapter 5.

9.3 Results and Discussion

The compounds modeled in this study are four late transition metal dioxides of RuO₂, RhO₂, IrO₂, and PtO₂, which are used in a number of

industrially relevant technologies.^{186,187} In addition to their stable rutile phase, possible polymorphs of anatase, brookite, columbite, and pyrite (Figure 9.1) are also modeled. Of these compound/phase pairs, only a few have been experimentally observed. RuO_2 has been observed in the pyrite-type phase at high pressure.^{188,189} A recent study correctly predicted the possibility of this polymorph using DFT and further proposed columbite and pyrite as possible synthesis targets of IrO_2 and RuO_2 .¹⁹⁰ Rutile-like $\beta\text{-PtO}_2$ is one of the three stable experimentally observed polymorphs of PtO_2 , though the structures modeled in this study have not been observed. RhO_2 has only been experimentally observed in a rutile like structure.¹⁹¹

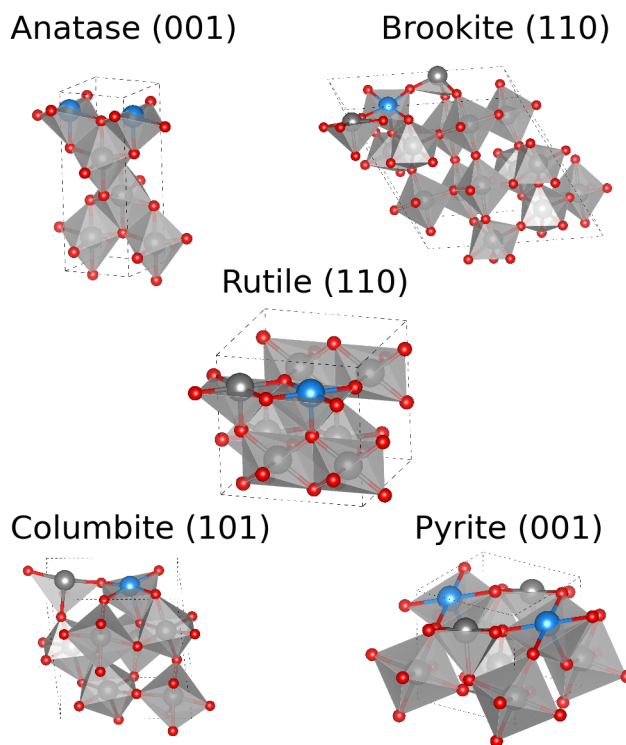


Figure 9.1: In addition to the stable rutile phase, the four metastable polymorphs used in this study. Images show the octahedral coordination present for metal cations found in all structures, along with the 5cus site used for all adsorption energy calculations. The periodic cell shown is the unit cell required for the construction of each specific surface.

In addition to being potential undiscovered synthesis targets, these polymorphs also allow one to isolate the effect structural distortions have on catalytic activity. Inspection of all crystal structures considered in this study reveals a similar octahedral coordination with six M -O bonds to all metal cations (Figure 9.1). Furthermore, all oxygen ions have a trigonal planar-like coordination, forming three O- M bonds for each oxygen anion. Hence, the local environment of both the cation and anion is similar across all structures, and all differences between polymorphs lie in structural distortions of bond lengths and angles. These distortions to the octahedral are similar to those observed by EXAFS in a number of experiments relating a distorted structure and different activity of TMOs for a number of reactions. [154,192–194](#)

The goal is to determine the effect these polymorph-induced distortions have on their reactivity. This is done by calculating both oxygen adsorption and vacancy formation energies. Vacancy formation energies are calculated in the bulk at the same vacancy concentration. While different crystal structures naturally produce a large number of different adsorption sites through geometrically different surface facets, this analysis is not the focus of this chapter. It is already well known that differences in coordination or stoichiometry of the surface adsorption site can produce significant differences in adsorption behavior. The objective of this work is to evaluate the effect that distortions to the MO_6 geometry have on the adsorption energy. To isolate the effect of distorting the MO_6 octahedral on the adsorption energy, adsorption sites on M ions are chosen to have the same number of missing bonds that maximizes the number of surface and sub-surface M -O bonds. This happens to be the 5cus site. The facets modeled that capture similar 5cus sites are shown in Figure 9.1, and DFT

studies show some of these surface facets are predicted to be thermodynamically stable.^{195–197} Note a study on the relative surface stabilities of the columbite structure could not be found, but calculations performed on columbite (101) show no major surface reconstructions. All adsorption calculations were calculated on these surfaces at the adsorption site shown in Figure 9.1.

The similar MO_6 environment of both the metal and oxygen ion in all crystal structures leads to the hypothesis that the M -O bond lengths should correlate with chemical properties. Differences in the M -O bond lengths between different crystal structures – or strain – should express itself as differences in the volume. Hence, in this study the strain of a specific MO_2 -polymorph is defined as the difference between the polymorph volume and the equilibrium volume of rutile MO_2 . Correlations between strain and adsorption and vacancy energies have been observed in a number of DFT studies.^{96,198} Figure 9.2 validates these correlations for rutile, showing smooth strain-dependent ΔE_{ads}^O and ΔE_{vac}^O . Surprisingly, adsorption on metastable polymorphs do not fall on these correlations. In addition, the changes in the adsorption energy caused by changing the crystal structure is oftentimes higher in magnitude than the change caused by straining rutile.

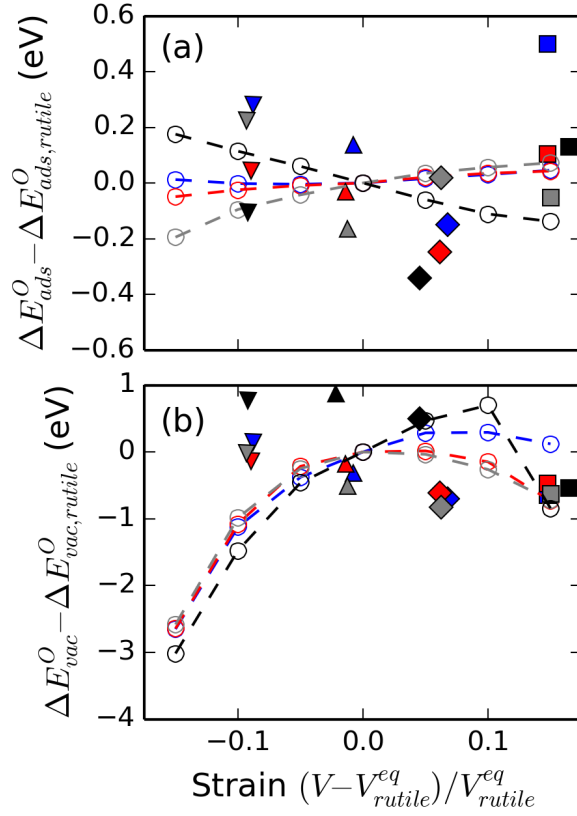


Figure 9.2: (a) Adsorption and (b) vacancy formation energies of all polymorphs and strained rutile plotted against the strain relative to the equilibrium volume of rutile of each respective element. Rutile is given by open $\bigcirc$ and the dashed lines connects rutile structures with different amounts of isotropic strain. Anatase, brookite, columbite, and pyrite are given by $\square$, ∇ , $\triangle$, and $\diamond$ markers, respectively. RuO_2 , RhO_2 , IrO_2 , and PtO_2 given by gray, red, blue, and black colored markers, respectively.

In contrast to adsorption energies, applying strain to rutile produces a much larger change in ΔE_{vac}^O than altering its crystal structure. Applying either compressive or tensile strain results in more exothermic vacancy formation, and ΔE_{vac}^O in polymorphs tend to be more endothermic than highly strained rutile. These results can be understood through structure stability. Straining rutile causes structural instability and allows for a greater degree of relaxation when a vacancy is created. In contrast, polymorph structures, which are fully relaxed at their equilibrium volume, are more

resistant to vacancy formation. This conclusion has important implications on the stability of these structures. A polymorph, though globally metastable, should have comparable stability in reactive environments where oxygen vacancies are regularly being created/filled. This result is consistent with studies where metastable structures were found to be stable in reactive conditions and showed structural-sensitive activity.^{160,161,163}

Correlations between adsorption energies and vacancy formation energies have been observed in past research and have ramifications on the balance of activity and stability of oxide materials.^{96,106,199} Figure 9.3 (a) shows correlations between adsorption and vacancy formation in the context of strain on rutile, but polymorphs do not follow these correlations. Furthermore, polymorphs exhibit a much larger degree of tunability of its adsorption energy without sacrificing stability. This observation motivates the search for polymorphs as possible candidates for breaking typical activity/stability trade-offs in catalytic operations.

To assess the potential catalytic activity of oxide polymorphs, adsorption energies of O, OH, and OOH are calculated with respect to the standard hydrogen electrode (SHE). Using a previously established atomistic thermodynamic framework summarized in Chapter 5, adsorption energies of O, OH, and OOH can predict the OER activity of catalysts.^{81,82} Consistent with previous results, Figure 9.3 (b) shows adsorption energies of O, OH, and OOH scale with each other, and adsorption energies on polymorphs fall on the same scaling as that of the rutile structures. This scaling persists most likely due to the similar geometric structure of the adsorption site, which has been observed to be a requirement on metal surfaces.^{200,201} Figure 9.3 (b) further demonstrates using structural sensitivity to tune adsorption energies,

where adsorption energies between those on stable rutile structures of different compounds are realized on polymorph structures.

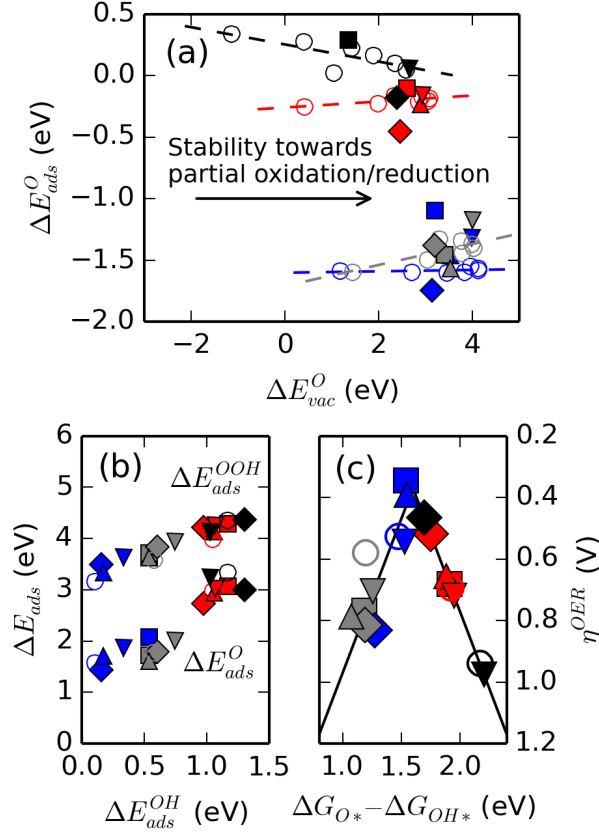


Figure 9.3: (a) Correlation between the adsorption and vacancy formation energy of all structures. (b) Scaling relationships between adsorption energies on O, OH, and OOH for all systems. (c) Theoretical overpotential towards oxygen evolution of all compounds. Rutile is given by open $\bigcirc$ and the dashed lines connects rutile structures with different amounts of isotropic strain. Anatase, brookite, columbite, and pyrite are given by $\square$, ∇ , $\triangle$, and $\diamond$ markers, respectively. RuO₂, RhO₂, IrO₂, and PtO₂ given by gray, red, blue, and black colored markers, respectively.

The ability of the polymorph to adjust adsorption energies along scaling relationships imply their activities should fall on the OER activity volcano and potentially give different activities with respect to rutile.⁸² This is shown in Figure 9.3 (c). Anatase and columbite IrO₂ and brookite RhO₂ and PtO₂ are predicted to be more active than their stable rutile forms. Work in the

Kitchin group suggests columbite IrO_2 as a potential synthesis target through thin film growth.¹⁹⁰ The present results further motivate experimental efforts to synthesize columbite IrO_2 .

While late transition metal oxide structures of anatase and brookite have been calculated to be high in energy and unfeasible to synthesize directly via either high pressure or thin film growth, TiO_2 is naturally occurring in both of these structures, easily synthesized, and stable under electrochemical and photochemical conditions.^{202,203} Furthermore, anatase and brookite TiO_2 have heightened photocatalytic activity and rutile TiO_2 can incorporate a large variety of transition metals as dopants.²⁰⁴ We therefore hypothesize Pt and Rh doped TiO_2 brookite or Ir doped TiO_2 anatase should increase photocatalytic water oxidation activity.

We stress again that the primary point of the OER analysis to assess whether structural distortions induced by polymorphs can produce significant changes in activity. Any reaction could have been chosen for this test, but OER was chosen due to the efficacy and simplicity of previously established models for evaluating catalytic activity^{82,90,205} and the usage of RuO_2 and IrO_2 as state of the art OER catalysts. These results motivate a more in-depth evaluation of the stability and activity of columbite IrO_2 , which includes the stability of several surface facets/terminations, activity of multiple adsorption sites, and a full potential energy landscape analysis.

Having demonstrated the unique activity and stability offered by potential polymorphs, we now investigate the origin of these properties by analyzing both the atomic and electronic structure. The case study performed to elucidate these structure-property relationships is IrO_2 in rutile, strained rutile, and columbite crystal structures. Figure 9.2 shows that rutile and columbite have similar equilibrium volumes and visualization

of their crystal structures reveal a similar hcp lattice of oxygen. Despite these similarities, changing the crystal structure from rutile to columbite produces a ~ 0.15 eV change in adsorption energy, while straining IrO_2 has negligible effects on adsorption.

Analysis of the atomic structure gives some insight into this effect. Table 9.1 shows the bond lengths and angles of Ir at the adsorption site on the rutile (110) and columbite (101) surface. Changes to bond lengths and angles produced by strain do not break the original symmetry of rutile, and no significant change of bond angles is observed of any rutile structures. Furthermore, strain induced bond length changes are not as high relative to the volume change, which is due to internal relaxations that reduce the effect of strain. In contrast, the columbite octahedral contains distortions relative to the octahedral found in the rutile crystal structure.

Table 9.1: Bond lengths and angles of strained rutile IrO_2 and columbite at the adsorption site. IrO_2^{R} , $\text{IrO}_2^{\text{R}+0.15}$, $\text{IrO}_2^{\text{R}-0.15}$, IrO_2^{C} refer to IrO_2 in the equilibrium rutile phase, rutile with 15% tensile strain, 15% compressive strain, and the columbite phase. $l_{M-O_{\text{sub}}}$ and $l_{M-O_{i=1,2,3,4}^{\text{surf}}}$ refer to bond lengths of the metal cation at the adsorption site with the single sub-surface and four surface oxygen anions, respectively. $\theta_{O_i^{\text{surf}}-M-O_j^{\text{surf}}}$ refers to the angle formed between two surface oxygen atoms and the metal cation at the adsorption site.

System	IrO_2^{R}	$\text{IrO}_2^{\text{R}+0.15}$	$\text{IrO}_2^{\text{R}-0.15}$	IrO_2^{C}
$l_{M-O_{\text{sub}}} \text{ (\AA)}$	1.950	2.102	1.865	2.028
$l_{M-O_1^{\text{surf}}} \text{ (\AA)}$	2.012	2.090	1.926	2.061
$l_{M-O_2^{\text{surf}}} \text{ (\AA)}$	2.012	2.090	1.926	1.913
$l_{M-O_3^{\text{surf}}} \text{ (\AA)}$	2.012	2.090	1.926	1.965
$l_{M-O_4^{\text{surf}}} \text{ (\AA)}$	2.012	2.090	1.926	1.893
$\theta_{O_1^{\text{surf}}-M-O_2^{\text{surf}}}$	74.6	76.9	72.1	97.5
$\theta_{O_2^{\text{surf}}-M-O_3^{\text{surf}}}$	104.9	103.1	107.9	84.3
$\theta_{O_3^{\text{surf}}-M-O_4^{\text{surf}}}$	74.6	76.9	72.1	89.8
$\theta_{O_4^{\text{surf}}-M-O_1^{\text{surf}}}$	104.9	103.1	107.9	88.1

The effect these structural changes have on the adsorption energy can be seen in the electronic structure. Figure 9.4 shows the atomic projected density of states of Ir at the adsorption site in rutile, strained rutile, and columbite IrO_2 . The striking feature that persists for all rutile structures is the shape and position of the t_{2g} -bands near the Fermi level, while the e_g -band undergoes significant changes to both the shape and positions upon strain. In contrast, the t_{2g} -band shape and position is significantly different for Ir in the columbite crystal structure when compared to any rutile DOS. IrO_2 columbite e_g -band has its low energy bonding and high energy anti-bonding orbitals at similar energy levels to IrO_2 rutile. Similar conclusions can be found for a majority of all other systems in this study.

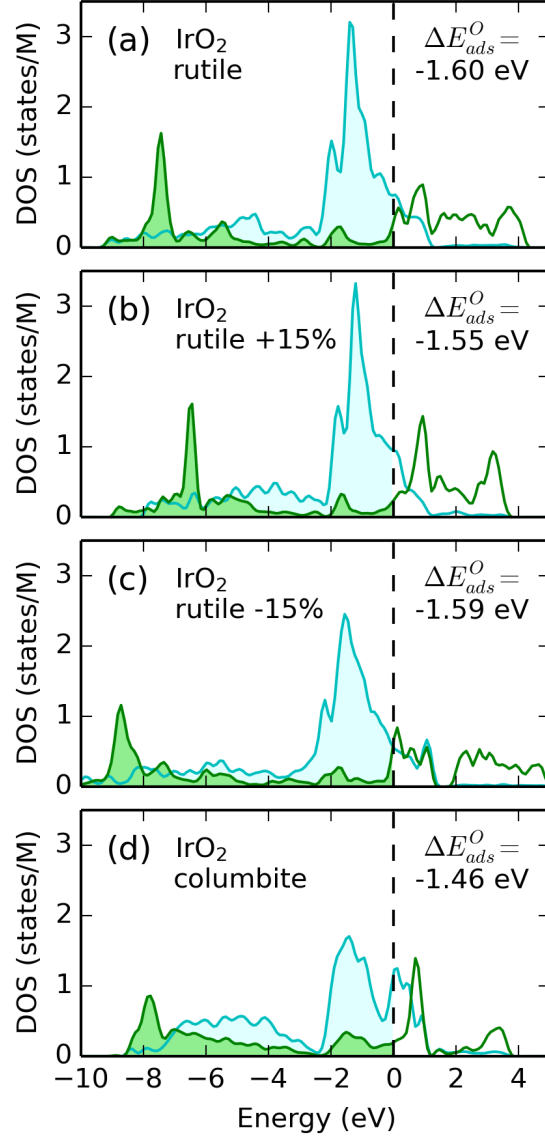


Figure 9.4: Density of states of rutile IrO_2 , rutile with maximum tensile and compressive strain. The green area represents the e_g states, and the cyan area represent the t_{2g} states. Filled areas represent the occupied electronic states below the Fermi level.

Two conclusions from the analysis of the changes in adsorption energy, atomic structure, and electronic structure in this case study are as follows: (1) the shape and position of the t_{2g} -states is vital for determining the strength of adsorption, and (2) distortions to M -O bonds within the octahedral geometry results in redistribution of the t_{2g} -band. Both of these

conclusions are surprising. Considering that the e_g -orbitals make σ -bonds with surface and adsorbate oxygen p -orbitals,²⁰⁶ the energy levels of the e_g -states should determine the bond strength. Likewise, distortions to the M -O bonds should express themselves as changes to the shape and energy levels of the e_g -bands. Results presented in this chapter show otherwise but are consistent with the results of Chapter 8 and recent work that show trends in adsorption energies can be correlated to the center of t_{2g} states near the fermi level.^{137,198} While universal correlations between properties of the electronic structure and the adsorption energy could not be found in this study, the higher ΔE_{ads}^O on columbite IrO_2 with respect to rutile IrO_2 most likely comes from the creation of high energy t_{2g} states at the Fermi level. Because these states are degenerate in energy with anti-bonding e_g -band, they are likely repulsive and serve to destabilize surface-adsorbate bond.

9.4 Conclusions

In light of the growing interest and ability to search structural space for new materials, the chemical properties of potential oxide polymorphs is explored. Changes to adsorption and vacancy formation energies on polymorph structures cannot be explained by strain alone. Oxide polymorphs are predicted to allow greater tunability in their adsorption properties while maintaining stability in reactive environments. This potential is highlighted by predicting certain polymorphs such as columbite IrO_2 to be more active for oxygen evolution and discussing their possible implementation. Analysis of both the atomic and electronic structure reveal distortions to the MO_6 octahedral geometry imparted through polymorphic structures causing significant redistribution of energy levels of the t_{2g} -states. Coupled with calculated adsorption energies, results in this chapter

emphasize the key role of the t_{2g} -states in determining the strength of adsorption.

10 Conclusions

The overall objectives of this dissertation were (1) developing DFT methods for calculating more accurate energetics of TMOs and (2) understanding how structure and composition of the TMO determines its activity. The two primary strategies used to accomplish these tasks were the linear response U and the calculated electronic structure. In the two following sections, the work done to accomplish each objective and future directions are summarized. The third section uses the successes of methods implemented in this dissertation to recommend research paths for the continued computational search for transition metal compound catalysts. The dissertation ends with brief concluding remarks.

10.1 Linear Response U for Accurate TMO Reaction Energies

10.1.1 Summary and Conclusions

Total energies calculated using DFT are the inputs to thermodynamic and kinetic models of catalytic processes. The accuracy of these total energies is a paramount issue. The fundamental source of inaccuracy in DFT calculations comes from electron-electron self-interaction error. Because useful thermodynamic and kinetic properties are *differences* in DFT calculated total energy values, one strategy to circumvent these issues is through cancellation of errors. However oxidation/reduction energies – the primary chemistry involved in TMO catalysis – contain remnants of non-canceling error. This error is associated with charge transfer associated with changes in the occupancy of d -electrons of the transition metal. The Hubbard U is a cheap correction one can add to correct self-interaction error.

The most common methods of choosing and using the Hubbard U limits its applicability for calculating TMO reactivity. Hubbard U values are typically chosen by fitting to experimental data, but adsorption energies on TMOs in reactive environments are difficult to measure. The self-interaction error and Hubbard U value is material specific, but an arbitrary energetic offset inherent in the Hubbard U precludes the comparison of total energies calculated with different U values.

In contrast to experimentally fitting to the Hubbard U , the linear response U is a method to self-consistently calculate the Hubbard U . In Chapter 3, development of the DFT+ $U(V)$ method enabled meaningful reaction energies with material specific U values. Using DFT+ $U(V)$, linear response U values were found to provide bulk oxidation energies of 3d TMOs with an accuracy comparable to state-of-the-art XC-functionals and fully empirical DFT+ U methods. In Chapter 4, linear response U was then extended towards bulk metal and 4d and 5d TMO energetics through the calculation of 3d, 4d, and 5d formation energies. Compared to 3d bulk oxidation energies, less improvement from using the linear response U and DFT+ $U(V)$ was found. Results discourage using linear response U on metals and motivates the continued development on 4d and 5d TMOs.

Motivated by increased accuracy of bulk TMO oxidation energies using linear response U , adsorption energies on TMO surfaces were calculated using a similar method in Chapter 5. With respect to TMO surfaces and oxygen containing adsorbates, three main conclusions were established. The application of any U results in more endothermic adsorption of O, OH, and OOH adsorbates. Endothermic shifts to adsorption preserved scaling relationships at $U = 0$. TMO activity trends for OER were improved with the application of the linear response U .

10.1.2 Future Directions in Solid-State Studies

While solid-state reactions like bulk oxidation and formation are less relevant to heterogeneous catalysis than reactions at the interface, these results have important ramifications toward a number of different disciplines. Materials discovery is required for the advancement of many technologies. The starting point of computational materials discovery is calculated bulk total energy values. Results in this dissertation suggest the linear response U can improve the accuracy of the relative stabilities of TMOs with different oxidation states. In addition, recent work from the Kitchen group found linear response U values correctly predicted the relative stability of TiO_2 polymorphs.²⁰⁷

Further development of linear response U routines will enable fast and accurate predictions of relative material stability. Development of linear response U techniques should be focused on the automation of linear response U calculations. Compared to the computationally expensive electronic convergence of hybrid-functionals, the linear response U calculation is relatively cheap. In contrast, current software and routines limit its applicability to case-by-case usage. For example, a python wrapper was written from scratch to automate the linear response U calculation and make possible the work done in Chapters 3 - 5.

In addition to the development of linear response U routines, the limits of linear response U should be tested. The Hubbard U was postulated as a computationally inexpensive correction to self-interaction error. Due to the ubiquitous nature of self-interaction error in DFT calculations, this postulate demands to be tested. Chapter 4 was an explorative study of that extended application of the linear response U to $3d$ TMOs to transition metals and $4d$ and $5d$ TMOs. Further studies on these materials and extensions to new

materials should be performed. A few studies from Wolverton and coworkers have tested the Hubbard U on transition metal sulfides and fluorides.^{28,208} Studies like these are increasingly more important as new transition metal compounds are at the forefront of materials development (see Section 10.3).

10.1.3 Future Directions in Interface Studies

In addition to the solid-state, Chapter 5 also suggest linear response U can lead to more accurate reaction energies at the interface. Work in this dissertation only looked at reactivity trends, but the results motivate benchmarking studies of comparisons between high quality linear response U adsorption energy calculations and experimental measurements on oxide surfaces. This benchmarking study should have DFT+ U (R) to be applied to adsorption energy calculations.

The method of applying the linear response U to surfaces should be further developed. Due to the symmetry present in many of the TMO studied in Chapters 3 and 4, a majority of the TMOs only required one linear response U . The creation of a surface and introduction of adsorbates will break this symmetry. A rigorous implementation of linear response U requires each unique TM have a linear response U , but this will likely be too computationally expensive. Progress should be focused on method development with the analysis of cost-benefit trade-offs with the linear response U .

Systematic changes to adsorption energies from the application of linear response U found in Chapter 5 should also be tested. The importance of systematic changes from the linear response U was previously discussed. The chemical similarity of the systems tested in Chapter 5 is a potential source to these systematic changes. All materials were TMOs and all adsorbates were

electronegative, oxygen containing species. These systematic changes are mirrored in the $3d$ TMO bulk oxidation and formation energies presented in Chapters 3 and 4, respectively. The similarities in all of these systems suggest that in an oxidation reaction, the linear response U results in a more endothermic reaction energy. However, preliminary results on transition metal sulfides suggest the trend is reversed in some cases. This also implies that the effect of U on an interface will also depend on the adsorbate. If relationships between the effect of U and the adsorbate can be found, the potentially expensive linear response U adsorption calculation can be avoided.

10.2 Electronic Structure for TMO Structure-Function Relationships

10.2.1 Summary and Conclusions

Behind calculated reaction energies are differences in the strengths of chemical bonds. Chemical bonds are made up of electrons, and the electronic structure provides all of the information required to understand the strength of a chemical bond. The chemical bond can be understood as the formation of new bonding and anti-bonding electronic states when orbitals of atoms overlap. For adsorption on extended surfaces, bonding and anti-bonding molecular orbitals form bonding and anti-bonding bands. When dealing with transition metals, the characteristics of the metal d -band describes trends in adsorption processes across not only the periodic table but also alloy space. Relationships between adsorption on the surface (chemical properties) and the metal d -band (electronic properties) has led to structure and composition sensitive models of catalytic activity.

Complexities of both the atomic and electronic structure in TMOs not found in metals hinder the physical understanding and development of analogous electronic structure models of TMO activity. These complexities arise from the introduction of oxygen into the metal lattice, which increases the diversity of bulk and surface structures and convolutes the electronic structure. Both of these challenges were addressed in this dissertation.

In Chapter 7, the foundation of knowledge built from over a decade of studying adsorption on metals was employed to understand adsorption on binary $3d$ TMOs. This was done by taking advantage of crystal structure motifs found in both fcc metals and rock-salt TMOs. In addition to identifying similar adsorption mechanisms on metals and oxides, two key conclusions directed work done on more structurally and complex diverse oxides in Chapters 8 and 9. The first is that key features of the electronic structure that described adsorption were dependent on whether the material was an early, mid, or late TMO. The second was the distribution of the TMO electronic structure into bonding, non-bonding, and anti-bonding bands that played different roles in adsorption. As a result, studies on ternary TMOs and polymorphs were focused on late transition metals and employed crystal field theory to spatially resolve the electronic states.

Investigations of adsorption on doped late $4d$ and $5d$ TMOs in Chapter 8 resulted in predictive electronic structure models that elucidated physics behind composition sensitive adsorption. Electronic structure models were built by identifying correlations between adsorption and the t_{2g} -band of the transition metal. Modifications to the t_{2g} -band through doping oxides could be understood through charge transfer between dopant and host atoms due to differences in atomic orbital radii. The effect of strain on adsorption in doped

oxides was an order of magnitude smaller than the effect of composition (ligand effect) and could be described by the idealized d -band filling.

The minor impact of strain on adsorption contradicted experimentally observed structure sensitivity of oxide catalysts. In Chapter 9, adsorption on polymorph oxides of compounds studied in Chapter 8 was studied. Polymorphs were chosen to maintain the same coordination but change bond lengths/angles of the transition metal, a phenomenon observed in many experimental studies. Compared to strain, results showed that polymorph oxides showed increased tunability of chemical properties (oxygen adsorption) and maintained stability (oxygen vacancy formation). Their potential as active catalysts was demonstrated through predicting columbite IrO_2 as more active for oxygen evolution than rutile IrO_2 . Similar to results found for doped oxides, changes to the t_{2g} -band were the most sensitive to changes to adsorption and the oxide structure.

10.2.2 Future Directions of Composition Sensitive Models

Novel materials with desirable catalytic properties will undoubtedly have compositions not previously tested. These compositions will likely include new combinations of elements that introduce new chemistry. The doped oxides studied in this system only capture a sliver of the potential interactions present in mixed oxides. These interactions include potentially more profound chemical effects like changes in the oxidation state from substitution of both metal cations and non-metal anions. The success of building a model to capture more subtle chemical effects in Chapter 8 suggests other effects can also be understood through analysis of the electronic structure.

The relevancy of a particular catalyst must also be rigorously studied. This requires the calculation of a large number of thermodynamic quantities, from bulk phase stability to adsorption induced surface segregation. These calculations are particularly pertinent if one considers the magnitude of calculated composition induced changes to the adsorption energy. For early transition metal, closed shell systems, the introduction of higher or lower valence dopants can induce up to 5 eV changes in adsorption.^{138,209} Even the doped oxides in Chapter 8 with chemically similar dopant-host pairs produced a dopant effect of up to a 1.5 eV change in adsorption energy. Similar observations of composition sensitivity of adsorption on metal surfaces are mitigated by a combination of surface oxidation, segregation, and adsorbate coverage effects. The identification of similar mitigating factors should be identified on oxide surfaces as well. It is also imperative that computational investigations of these effects be done in collaboration with experiments. Compared to the measurement of adsorption energies on oxide surfaces, phenomenon of surface oxidation, segregation, and coverage are typically easier to observe and qualitatively compare to first-principles calculations.

10.2.3 Future Directions of Structure Sensitive Models

Tailored structure-tuning of the active sites of catalysts is typically more difficult than changing the composition. A growth in the expertise of experimentalists has elevated the ability to characterize and synthesize structurally novel materials. Synchrotron techniques can provide high fidelity structural data such as bond lengths and angles. Active developments in microscopy tools have resulted in unprecedented resolutions of surfaces of materials. Synthesis techniques are continually being shifted to the

nano-scale, and work on metal nano-materials have resulted in a number of metastable geometries exposing previously inaccessible active sites.

Better experimental tools for identifying and realizing active sites motivates an analogous ability to computationally predict structure sensitivity of chemical reactions. Both the complexity and diversity of TMO structures lead to a plethora of potential geometrically unique surface structures and adsorption sites. Results in Chapter 9 suggest even mere changes to bond lengths and angles while keeping a fixed coordination environment could lead to substantial changes in activity.

Results from Chapter 9 motivates two research directions. The first is that the active site of structurally complex and diverse materials could look quite similar. If these similarities could be efficiently identified, models of catalytic activity that span structural space could be built. These results motivate the development of routines for surface creation and smart categorization of active sites.

The second research direction regards the creation of structural-sensitive models of catalytic activities. The complexity of oxide structures leads to high-dimensional input data to any structural model. Early models predicting activity of an active site in an alloy only required the distances to neighboring atoms.¹¹⁴ Results from Chapter 9 suggest a similar model would not be sufficient, where changes to the geometry around the active site produced non-trivial changes to the electronic structure and activity.

One way to handle complex, high-dimensional structural input data is through machine learning. In contrast to physics based models where a combination of physical intuition and trial-and-error is required, machine learning uses large amounts of data and intelligent fitting procedures to generate suitable models. The atomic structure is an ideal data set for

training machine learned models. One popular structure-sensitive, machine-learned model is the Behler-Parrinello neural network.²¹⁰ This model has been proven to be effective for predicting the structure of a number of bulk and surface systems.^{210–212} It should be tested whether a similar neural-network could relate the active site geometry and activity.

10.3 Computational Engineering of Complex Catalysts: General Principles from TMOs

The third section of this chapter uses the the work done in this dissertation to motivate general research principles of the computational engineering of transition metal compound catalysts. The field of computational catalysis has seen explosive growth in the past decade. A majority of the work has been done on more simple catalysts. These include chemical reactions on metal surfaces, where the structural homogeneity across compositions allows for the easier implementation of screening studies across alloy space. Hence, a great amount of progress has been seen in chemical reactions that take place in highly reductive environments where an oxide is not thermodynamically favored. Progress in the catalytic trends across compositional and structural space include H₂ evolution,^{77,213} O₂ reduction,^{214–216} CO hydrogenation,^{117,217} CO₂ reduction,²¹⁸ and NH₃ synthesis.²¹⁹ Many of the state-of-the-art catalysts are currently being optimized on the nano-scale through shape, size, and composition engineering.

Moving forward, novel active materials will most likely encompass transition metal compounds. A few examples of recently discovered active transition metal compound catalysts for replacing noble metals highlight their potential. MoS₂ was identified as an active H₂ evolution catalyst.²²⁰ A

number of perovskites have found to be active for O_2 reduction in alkaline environments.²²¹ Metal carbides have found to have comparable activity and stability to noble metals for CO hydrogenation.²²² Compared to noble metals where current effort is focused on nano-structure engineering, there are still new materials to be discovered for transition metal compounds.

The investigations on TMOs catalysts in this dissertation presents three successful research strategies for studying transition metal compound catalysts. The first is that the understanding on familiar systems should serve as a foundation for understanding more complex systems. In Chapter 3, the development of the DFT+ $U(V)$ method was inspired by very similar calculations on molecules, where a DFT+ $U(R)$ method validated the linear response U for FeO^+ dissociation energies. The identification of key electronic features of binary TMOs in Chapter 7 was not possible without the depth of understanding of adsorption on metals. The ligand and strain effect introduced for doped oxides in Chapter 8 have obvious parallels with identically named interactions in thin-film metal catalysts.

Second, computational scientists have the luxury of calculating "imaginary" systems. While experimental corroboration is strongly encouraged of all DFT calculations, the ability to model whatever one desires should be exploited when appropriate. Expanded bulk lattice calculations performed in Chapters 3 and 7 are unstable systems which are not remotely similar to any experimentally observed materials. However, the calculation of such systems enabled the construction of the semi-empirical DFT+ $U(V)$ method and connected adsorption mechanisms on metals and oxides. Artificially strained systems in Chapter 8 identified the ligand effect as the dominant mechanism in doped oxides. Polymorphs studied in Chapter 9 – many of which have been previously predicted to be experimentally

unattainable – magnified the impact mere changes to TMO bond lengths and angles can have on the adsorption energy.

The third research strategy is the continual need for computational chemical engineers to become experts in both physics and materials science. A major and fruitful research strategy proven to be effective is the search for descriptors in describing trends in heterogeneous catalysis. These descriptors are often adsorption energies and hence are focused on the active site of the catalyst. However, recent experimental studies have shown that other material properties are vital for determining activity. One example is the impact of bulk conductivity on electrocatalysts. Only recently has the origin of the active Fe-Ni oxide oxygen evolution catalyst, first discovered in 1980,²²³ been identified as Fe active sites embedded in a conductive NiO_x crystal. The surface activity and bulk conductivity have been independently tuned in recent work looking at transition metal compounds of Ni selenide²²⁴ and phosphides.^{225,226}

Physics and materials science expertise were required in a number parts of this dissertation. Before the work done in this dissertation, the linear response U was almost exclusively used in the study of non-thermodynamic quantities and saw no use in evaluating energetics of heterogeneous catalysis. The DFT+ $U(V)$ method was engineered to prove its effectiveness for calculating quantities relevant to chemical engineers. Furthermore, the question raised in Chapter 4 of whether linear response U should be applied to $4d$ and $5d$ TMOs could be addressed by performing a more physics or materials science based investigation. An understanding of crystal field theory was required to break up the convoluted electronic structure of TMOs into e_g and t_{2g} -bands. Similar qualitative relationships between the material

and the electronic structure from crystal field theory should precede and interpret DFT calculations.

10.4 Concluding Remarks

The future is bright for the computational design of catalysts. This dissertation shows that the initial high output of advances in science and engineering on transition metal catalysts is not likely to slow down as engineers search for more complex materials. Previous sections of this conclusion chapter were centered on using results and methods of this dissertation to motivate the direction and strategies of future research. The final section will highlight how certain "deficiencies" of work in this thesis hint at the scope of future work in computational catalysis.

One remarkable observation is the relative dearth of systems studied in this dissertation. All adsorption studies carried out in this work were done on a relatively small set of systems. Chapters 5 and 8 only looked at the ideal, stoichiometric (110) surface of transition metal rutile dioxides. Chapter 7 only looked at the (111) surface of rock-salt TMOs. Adsorption on oxide polymorphs studied in Chapter 9 – a majority of which have never been computationally studied as potential catalysts – were limited to a single adsorption site on a single termination of a single facet. Oxides studied in this dissertation by no means encompasses the potential TMOs to be discovered let alone the current state-of-the-art TMO catalysts. However, given such a limited pool of TMOs studied, a number of novel structure-function relationships were uncovered. It is likely countless more relationships are awaiting to be discovered as one approaches more transition metal compound catalysts and reactions.

There is also a noticeable lack of collaboration done to produce the work in this dissertation. Some of the calculations in Chapter 4 were run by collaborators, but all of the original scripts used to generate and analyze the results were written solely by the author. However, the amount of progress made in this dissertation on studying TMOs barely touches on the potential progress possible from collaboration with experts in other fields. One obvious collaboration would be with experimental chemists and chemical engineers who can synthesize and test new catalysts. In addition, expertise in areas of physics, materials science, computational science, and optimization will be crucial as one searches for catalysts with new physical and chemical phenomenon with continuously increasing computational resources.

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rrkjus.UPF, Co.pbe-nd-rrkjus.UPF, and Ni.pbe-nd-rrkjus.UPF from <http://www.quantum-espresso.org>.

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