# UNTANGLING COMPLEXITIES OF SELECTIVE CARBON-OXYGEN BOND ACTIVATION USING MULTISCALE MODELING AND QUANTUM THEORY DEVELOPMENT

by

Alexander V. Mironenko

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

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#### ABSTRACT

Selective carbon-oxygen bond activation in  $C_{2+}$  molecules represents an essential part of the carbon-neutral, solar energy-based economy of the future. In biomass-mediated pathways, the initial CO<sub>2</sub> reduction and C-C coupling are carried out through biochemical photosynthesis in photoautotrophic organisms. The resulting chemicals and bioproducts are typically over-oxygenated. Subsequently, selective C-O bond scission in fatty acids, glucose, glycerol, and furans is conducted to remove some of the excess oxygen. Despite a plethora of proposed heterogeneous catalysts, the C-O activation mechanism and peculiarities of catalyst reactivity remain poorly understood.

In this thesis, we report the discovery of a radical-mediated C-O bond activation mechanism on the multifunctional Ru/RuO<sub>x</sub> catalyst that enabled 2-methyl furan production from furfural with up to 76% yield at temperatures  $<200^{\circ}$ C. To the best of our knowledge, this was the first evidence of a low-temperature radical *reduction* mechanism in heterogeneous catalysis. The breakthrough was made possible by extensive exploration of various catalytic site architectures and reaction mechanisms using density functional theory, together with microkinetic modeling that showed agreement with experiment in both ultrahigh vacuum and liquid phase, thus bridging the pressure gap.

Through collaborative experimental/computational work, we show the mechanism generality by identifying a wide range of reducible oxides that can catalyze the C-O bond scission on vacancies. Moreover, we find reactivity trends for

saturated vs. unsaturated compounds to be fully consistent with computational predictions regarding the positive effect of conjugation on C-O bond scission rates.

We obtain computational evidence that a similar mechanism is at play on 3-4 nm PtCo nanocrystals, covered with a  $CoO_x$  monolayer, and is responsible for ultrahigh yields (99%) of 2,5-dimethylfuran from 5-(hydroxymethyl)furfural. The catalyst structure and the reaction mechanism are fully consistent with EXAFS, XANES, XRD, TEM, chemisorption, and reactivity data.

Advancements in mechanistic understanding were made possible by development of first principles microkinetic models, specifically designed to simulate experiments involving isotopically labeled species and to predict mass fragmentation patterns. Initial work led to the discovery of the ring-opening deuteration mechanism that shed light on the roles of substituent groups and of solvent on deuteration rates of furanics. The mechanism was in stark contrast to the commonly known Brønsted acid-catalyzed mechanism.

Over the course of our studies, we encountered challenges associated with reliable reaction rate predictions on metal oxide catalysts, revealing deficiencies of current quantum mechanical methods. To address them, we propose a non-empirical quantum-theoretical framework, aimed to describe electronic structure of such materials more accurately. Remarkably, the rigorous quantum theoretical basis of the method makes it applicable also to molecules and metals, demonstrating a consistently improved description of chemical bonding across the chemical compound space. The newly developed method holds promise to make first principles predictions in catalysis, especially metal oxide catalysis, more reliable and at minimal extra computational cost.

#### Chapter 1

#### **INTRODUCTION**

#### 1.1 Complexity in Catalysis

Catalysis is an indispensable, enabling science for solving energy and environmental problems. Waste water treatment, sustainable production of basic chemicals, carbon dioxide conversion to liquid fuels – progress in such vital areas critically depends on transformative development of new solid materials, capable of selectively activating chemical bonds.

For the most part of the 20<sup>th</sup> century, rapid catalyst discoveries were hindered by the significant amount of trial and error involved. Simplest chemistries, such as ammonia synthesis, demanded thousands of experiments, in order to identify the most promising catalyst candidates and optimal reaction conditions.<sup>6</sup> Catalyst characterization techniques facilitated catalyst search through approximate structurereactivity relationships, by accessing bulk (x-ray diffraction and absorption) or surface (x-ray photoelectron spectroscopy, in-situ infrared spectroscopy, chemisorption, etc.) structure of the catalyst active phase. However, insufficient atomic resolution and lack of one-to-one correspondence between spectroscopic fingerprints and reaction rates deemed the prediction of new catalysts a nontrivial task.

Difficulties with describing catalytic phenomena are attributed to the complexity of processes on catalyst surfaces (Figure 1.1). A multitude of reactions and reaction intermediates may appear in seemingly simple transformations – for example, there are 464 possible reactions in *para*-cresol hydrodeoxygenation on Pt.<sup>7</sup> Several

catalytic sites can be simultaneously present and act in a concerted manner.<sup>8</sup> A catalyst may undergo phase change and restructuring under reaction conditions or during preparation.<sup>9</sup>



Figure 1.1. Complexity in heterogeneous catalysis.

Finally, a solvent may either modify energies of reaction intermediates<sup>10</sup> or act as a reactant.<sup>11</sup> Experimental catalyst characterization methods can only provide space- and time-averaged information, and the atomic resolution can only be achieved at ultrahigh vacuum or low-pressure reaction conditions on ideal surfaces (as in scanning tunneling microscopy), not representable of industrial processes. Fortunately, rapid progress in computational power and simulation methodology over the last 50 years brought about modeling approaches that link atomic features to macroscopic observables<sup>12</sup>, bridging pressure and material gaps.

#### **1.2 Multiscale Modeling**

On the most fundamental level, all chemical processes in Nature can be regarded as solutions to the many-body problem, described by the Schrodinger equation.<sup>13</sup>. Due to exponential increase of the computational cost with the number of particles (electrons, atomic nuclei), its direct solutions are impractical or impossible, necessitating approximate methods. Semilocal density functional theory (DFT)<sup>14</sup> is the most frequently used approximation, due to the high accuracy-to-cost ratio. It enables accurate determination of the potential energy surface (PES), i.e., the system energy as

a function of atomic coordinates, from which atomic trajectories can be obtained (Figure 1.2). Trajectories, in turn, can be linked to macroscopic observables (reaction rates, spectrometric signals) through the statistical mechanical formalism.



Figure 1.2. Information flow in multiscale modeling.

The information flow, depicted in Figure 1.2, suggests the following modeling strategy in catalysis – one constructs a set of catalytic models, relevant to specific chemistry, and calculates their corresponding macroscopic observables, e.g., reaction rates. Then, a mechanistic study is performed for the most relevant structure, which yields the best agreement with the experiment. Unfortunately, this direct strategy is infeasible, since even approximate quantum mechanical methods cannot deal with an order of the Avogadro number of atoms, and thus further approximations are required.

Due to the short-range character of interatomic interactions, distant parts of a catalyst can be regarded as independent; they are referred to as *catalytic sites*. Catalytic sites involve dozens of atoms and thus are computationally tractable. Although DFT can yield atomic trajectories, in practice only very short times can be accessed computationally (picoseconds), missing many slow reactions. An alternative is to take advantage of the Boltzmann distribution and compute not the entire PES, but only a handful of its special points – local energy minima and saddle points. Local minima are then associated with chemical species – reaction intermediates; computation of their thermodynamic properties involves a PES in the immediate vicinity of minima, and thus, it is computationally feasible. In Eyring's transition state theory,<sup>15</sup> saddle points are referred to as transition states; they correspond to transitions between different PES minima, and knowledge of their energies allows for calculation of rate constants of surface chemical reactions.

Once equilibrium and reaction rate constants are computed, one can take advantage of the fact that, if the number of catalytic sites is large, their collective behavior can be regarded as continuous, and thus one can construct and solve a system of differential equations for the pre-assembled reaction network. Since atomic coordinates do not enter the equations, modeling of a chemical system over much longer, experimentally relevant times is feasible, from which macroscopic reaction rates can be extracted. A combination of different methodologies applicable to different time and length scales is referred to as multiscale modeling. In this thesis, we employ it to obtain insights into catalytic reactions of environmental importance.

#### 1.3 Catalytic Biomass Upgrade

There is a consensus among 97% of climate science experts<sup>16</sup> that excessive  $CO_2$  emissions are the main contributor to the ongoing climate change and its associated economical and human life risks.<sup>17</sup> According to Steven Chu, a Nobel Prize co-winner in Physics'97, economically competitive carbon recycling via conversion of  $CO_2$ , water, and solar energy to high-energy-density  $C_{2+}$  liquid fuels is the ultimate solution to the climate change problem.<sup>18</sup> Transformation of  $C_1$  species to  $C_{2+}$  fuels and value-added chemicals is challenging, due to associated high capital costs (Fischer-Tropsch<sup>19</sup>), or selectivity issues owing to fundamental constraints in metal catalysis.<sup>20</sup> However, Nature is quite efficient in converting  $CO_2$  to complex molecules (biomass) by means of photosynthesis. In the absence of an efficient  $CO_2$ -to-chemicals/fuels process, the next best solution is to consider biomass, rather than  $CO_2$ , as a starting point for subsequent chemical reactions.



Figure 1.3. Biomass conversion pathways.

Among various biomass resources, lignocellulosic biomass is particularly valuable due to its abundance in agricultural and municipal waste and paper production byproducts. In addition, its production routes do not compete with the food chain. The primary lignocellulosic biomass constituents are cellulose, hemicellulose, and lignin biopolymers. Unlike complex and very stable lignin, cellulose and hemicellulose are much more amenable to transformations at mild reaction conditions.

Cellulose and hemicellulose can be depolymerized in the acidic environment, forming their respective monomers glucose and xylose (Figure 1.3). Both monosaccharides contain a large number of nucleophilic OH groups, which are prone to proton attack, leading to unselective dehydration. However, the five-member ring of xylose is converted to the aromatic, thermodynamically stable furan ring, which acts as a thermodynamic sink, leading to 90-95% selectivities in furfural production.<sup>21</sup> Glucose can be converted to fructose via hydride transfer on Lewis acidic catalysts;<sup>22</sup> considerable amount of fructose exists in a furanose form (5-member ring), thus its subsequent conversion to 5-(hydroxymethyl) furfural (HMF) also benefits from the aromatic stabilization. High HMF yields can be achieved, especially when dehydration is coupled with HMF extraction in a biphasic reactor.<sup>23</sup>

Furfural and HMF are too reactive and must be stabilized by hydrodeoxygenation (HDO), forming 2-methyl furan (2MF) and 2,5-dimethylfuran (DMF), respectively. Due to the unprotected  $\alpha$ -carbon, 2MF can participate in acylation reactions, e.g., with furfural, forming larger molecules with unique structure, different from typical petroleum molecules. Such biomass-derived large molecules were found to be good lubricants with very low pour points,<sup>24</sup> demonstrating the biomass potential as a source of novel and unique products.

DMF can be either used as a fuel, or can be converted to valuable chemicals, analogous to those in petroleum. Due to hyperconjugation, C-H bonds in methyl group are weak and thus can be readily oxidized, forming 2,5- furandicarboxylic acid, which can be ultimately converted to a precursor for nylon – adipic acid.<sup>25</sup> DMF can also participate in Diels-Alder reaction, enabled by the positive inductive effect of methyl groups, ultimately forming p-xylene. The latter, in turn, can be oxidized to terephthalic acid, a precursor to polyester PET.

In this thesis, we focus on only one reaction type in Figure 1.3 - C-O bond activation.

#### **1.4 Dissertation Scope and Structure**

In Chapter 2, we analyze interactions of furan compounds with a Ru surface to elucidate the effect of substituent groups on the experimentally observed H/D exchange rates. In Chapter 3, we move to a more complex catalytic system and describe the discovery of a trifunctional mechanism of C-O bond activation on the mixed Ru/RuO<sub>2</sub> catalyst. In Chapter 4, we generalize the mechanism to other reducible metal oxides, for which experimentally relevant surface terminations and surface reactivity descriptors are elucidated. In Chapter 5, we report a similar mechanism on the surface of CoO<sub>x</sub>-covered PtCo nanocrystals. We develop a mean field-type structural model, which allows us to come up with the catalyst structure in complete agreement with all pieces of experimental data available. Chapters 2-5 employ conventional semilocal DFT methods, which have limitations for the chemistry of oxides. In Chapter 6, we discuss the shortcomings of various DFT functionals available and review quantum mechanical and DFT principles. In Chapter 7 we make use of theoretical concepts of Chapter 6 to derive a new non-empirical DFT functional. We report the method formalism, as well as curious regularities and very promising results for realistic systems. In Chapter 8, we summarize the dissertation conclusions and provide future research directions.

#### Chapter 2

#### RING ACTIVATION OF FURANIC COMPOUNDS ON RU-BASED CATALYSTS

#### 2.1 Abstract

We employed a combination of isotopic labeling experiments, density functional theory calculations, and first-principles microkinetic modeling to investigate the mechanism of H/D exchange of furanic platform molecules. Alkylated furans (e.g., 2-methylfuran (2-MF)) exhibit appreciable H/D exchange but furan and oxygenated furanics (e.g., furfuryl alcohol) do not. Detailed mass fragmentation pattern analysis indicates H/D exchange only occurs at unprotected α-carbons. Simulations show that in the presence of co-adsorbed toluene (solvent), the most likely pathway involves Ru-surface mediated scission of the C-O bond in the furan ring at the unsubstituted carbon atom, followed by dehydrogenation, deuteration, and ring closure steps. The degree of H/D exchange reaction depends mainly on the adsorption strength of exchange intermediates: Strongly bound compounds, e.g., furan and FA, inhibit H/D exchange via site blocking and slow desorption, whereas alkylated furans are sterically repelled by the solvent freeing up catalysts sites for exchange at the unsubstituted  $\alpha$ -carbon of the furan ring. The binding strength of exchange intermediates is governed by interaction of the substituent group both with the surface and with the co-adsorbed solvent molecules. The proposed H/D exchange mechanism on metal catalysts, which involves the opening of furan ring, is in stark contrast to the Brønsted catalyzed ring activation and suggests a possible pathway for the formation of ring opening products and for rational selection of solvents.

#### 2.2 Contributions

Alexander V. Mironenko performed density functional theory calculations and developed microkinetic models of H/D exchange. Matthew J. Gilkey, Paraskevi Panagiotopoulou, and Gregory Facas carried out isotopic labeling experiments. Dionisios G. Vlachos and Bingjun Xu guided computational and experimental research, respectively.

#### 2.3 Introduction

Biomass is the only renewable carbon source and its chemical makeup renders it ideal for the production of C<sub>4</sub>-C<sub>8</sub> chemicals. Unlike fossil fuels, the composition and molecular structure of biomass derivatives are highly diverse, requiring a myriad of strategies for the design of catalysts and reactors. However, developing many distinct processes for upgrading different types of biomass imposes a hefty economical penalty for the sustainable production of biochemicals and biofuels. One effective strategy is to convert different biomass feeds to a handful of "platform chemicals",<sup>26</sup> to which a common upgrade strategy can be applied. Furanic compounds, e.g., 5hydromethylfurfural (HMF) and furfural, are such platform chemicals,<sup>27,28</sup> and effective bio- and thermo-catalytic processes have been developed for their production and upgrade in the last decade.<sup>29-32</sup> Comparing with petroleum, biomass-based feedstocks contain a high content of oxygen, and a common strategy for their upgrade is hydrodeoxygenation (HDO), i.e., removing oxygen-containing functional groups by adding hydrogen via hydrogenation and hydrogenolysis.<sup>33</sup> Significant progress has been made in HDO of oxygenated furanics to alkylated furans. Ru-based catalysts have shown remarkable activity in the HDO of HMF and furfural to reduced furans 2,5-dimethylfuran (2,5-DMF) and 2-MF, respectively, either using high pressure H<sub>2</sub><sup>34</sup> or via catalytic transfer hydrogenation with alcohols as hydrogen donors <sup>35-38</sup>. Our recent studies show that mildly oxidized supported Ru catalysts are most active in the HDO of HMF and furfural, and the coexistence of both metallic Ru sites and Lewis acid sites, i.e., a RuO<sub>x</sub> phase, is key to reach high yield of 2,5-DMF and 2-MF<sup>35-37</sup>. Further upgrade of alkylated furans to valuable chemicals, such as 1,6-hexanediol, requires activation of the aromatic furan ring, such as ring hydrogenation<sup>39</sup> and ring opening.<sup>40,41</sup> Molecular level understanding of the adsorption and activation of furan ring on metal surfaces, a key prerequisite for rational catalyst design, is though still lacking. In addition, solvent effects on biomass upgrade are in general poorly understood.<sup>42</sup>

Herein, we present a combined experimental and computational study to identify the mechanistic steps in the activation of the aromatic ring of several model furanic compounds on Ru-based catalysts. The employment of isotopically labeled hydrogen donor (isopropanol- $d_8$  (IPA- $d_8$ )) and detailed mass fragmentation analysis reveal that the incorporation of deuterium in the furan ring occurs on the unprotected  $\alpha$ -carbon. A combination of DFT calculations and first-principles microkinetic modeling (MKM) indicates that, unlike unsaturated hydrocarbons, ring opening/closing mechanism is responsible for the H/D exchange on the furan ring. Furthermore, we show that solvent effects, rather than electronic effects of ring substituents, dictate the relative rates of H/D exchange of various furanics.
## 2.4 Methods

### 2.4.1 Experimental

## 2.4.1.1 Reaction Conditions and Analysis

Reactions in this work were conducted in a 100 mL stainless steel Parr reactor. In each experiment, the reactor was loaded with 1 wt% reactant (with 99% purity, Sigma Aldrich) in a 24 mL IPA (or IPA- $d_8$ , Sigma Aldrich, 99.5 mol % D) and toluene solution (10% IPA or IPA- $d_8$  by volume), 100 mg of pre-treated Ru/C catalyst, and a magnetic stir bar. Once sealed, the reactor was subsequently purged with nitrogen gas 3 times before pressurizing the vessel to 300 psig with N<sub>2</sub>. After preparation, the reactor was immediately placed in a heated oil bath for a reaction time of 5 hours.

## 2.4.1.2 Catalyst pre-treatment

Ru/RuO<sub>x</sub>/C catalysts were pretreated in sequential reduction and oxidation steps in a quartz flow reactor packed with 5% Ru/C (Sigma-Aldrich). The reduction of the catalyst was conducted in a mixture of He/H<sub>2</sub> (20/20 sccm) at 300 °C for 3h. Then the catalyst was allowed to cool to room temperature under He flow (40 sccm) before switching to an O<sub>2</sub> and He mixture (3.6/36.4 sccm) and heating to 130 °C for 3h. Reduced Ru/C catalysts were prepared by reducing 5% Ru/C under identical conditions to that of Ru/RuO<sub>x</sub>/C catalyst; however, it is not followed by the oxidation step. RuO<sub>2</sub> (Sigma Aldrich) catalysts were pretreated at 200 °C for 2 h in He (40 sccm).

# 2.4.2 Computational

# 2.4.2.1 Density Functional Theory (DFT) Calculations

Reaction energies and activation barriers were determined using DFT implemented in the Vienna ab initio simulation package (VASP) code, version 5.3.3<sup>43-46</sup>. Interactions between ionic cores and valence electrons were modeled using the projector-augmented-wave method<sup>47,48</sup>. The Kohn-Sham equations were solved using a plane wave basis set with a kinetic energy cutoff of 400 eV. Electronic density at each ionic step was determined self-consistently with an energy tolerance of 10<sup>-4</sup> eV. Decrease of the tolerance to 10<sup>-6</sup> resulted in energy changes of less than 0.005 eV. Exchange-correlation effects have been estimated using a generalized gradient approximation (GGA) as implemented in the Perdew, Burke, and Ernzerof energy functional (PBE)<sup>14</sup> with Grimme's dispersion correction, D3<sup>49</sup>. The latter was found to be essential for better estimation of chemisorption energies of furans <sup>50</sup>.

Bulk calculations were performed using a tetrahedron method with Blochl corrections and  $15 \times 15 \times 15$  Monkhorst-Pack k-point mesh<sup>51,52</sup>. The bulk lattice constant of Ru was obtained using Birch-Murnaghan equation of state<sup>53,54</sup>. The hcp Ru lattice constant was found to be a = 2.6958 Å with a c/a ratio of 1.5815, which is close to the experimental values a = 2.7058 Å and c/a = 1.5824<sup>55</sup>.

The Ru(0001) metal surface was modeled with a 4×4 unit cell composed of four atomic layers (a 6×4 unit cell was used to in the presence of toluene; see appendix). The bottom two layers were fixed at interatomic distances corresponding to the bulk phase, whereas the two uppermost layers and any adsorbate were allowed to relax. The vacuum thickness between slabs was set to 20 Å. The first Brillouin zone was sampled with a  $3\times3\times1$  k-point mesh. Total energies were determined using the

Methfessel-Paxon method with a smearing parameter of  $0.1^{56}$ . The conjugate gradient method was used for energy minimization. Ionic relaxation was performed until the Hellmann-Feynman forces were lower than 0.03 eV/Å. Adsorption energies of all intermediates were computed with respect to the gas phase energy of a corresponding reactant and hydrogen atoms adsorbed on separate slabs as the following:

$$\Delta E_{ads} = (E_{slab+ads} - E_{slab}) - E_{r,gas} - z \times (E_{slab+H} - E_{slab})$$
(2.1)

Here  $E_{slab+ads}$  is the energy of the slab with an adsorbed molecule on it,  $E_{slab}$  is the energy of a clean Ru slab,  $E_{r,gas}$  is the DFT energy of a relaxed stable reactant in the gas phase,  $E_{slab+H}$  is the energy of the slab with an adsorbed H atom on it, and z is the number of H atoms required to be removed from the stable reactant molecule to form a particular intermediate. The supercell for all gas-phase calculations was chosen to be  $20\times21\times22$  Å, and the first Brillouin zone was sampled at a single  $\Gamma$  point. Spin polarization was accounted for in the gas-phase calculations and was turned off for slab calculations. Including the spin in slab calculations did not change the total energy by more than 0.02 eV.

Vibrational frequencies of stable species and transition states were obtained under the harmonic approximation by diagonalizing the Hessian matrix. Second-order partial derivatives were calculated using numerical differentiation of forces with a step size of 0.015 Å. To reach high accuracy and avoid spurious negative frequencies, electronic energy tolerance was decreased to  $10^{-6}$  eV. In the vibrational analysis, all metallic atoms were held fixed, whereas all atoms of an adsorbate were allowed to relax.

Transition states were found using the Climbing Image Nudged Elastic Band method (CI-NEB) <sup>57-62</sup> with 10 images equidistantly located along the reaction

pathway. All transition states were verified by harmonic vibrational analysis as having only a single imaginary frequency.

## 2.4.2.2 First-principles Microkinetic Model (MKM)

Microkinetic models were set up using an in-house CHEMKIN<sup>TM</sup>-based Fortran code <sup>63,64</sup> as described elsewhere<sup>65</sup>. The simulation has been carried out in a batch reactor with the same volume and catalyst amount as used in the experiment. The include IPA dehydrogenation elementary steps to acetone. ring (de)hydrogenation, ring opening at the  $C_2$ -O and  $C_5$ -O positions followed by hydrogenation and dehydrogenation steps in this or reverse sequence, and finally ring closing. The pathways explored are discussed below. The parameterization of the microkinetic model is detailed in Section A.1.

# 2.5 Results and Discussion

# 2.5.1 Furan Ring Activation of 2-MF on Ru/RuO<sub>x</sub>/C

Furan ring activation occurs upon reacting 2-MF with IPA- $d_8$  on Ru/RuO<sub>x</sub>/C, as evidenced by the incorporation of deuterium (D) into 2-MF after reaction with IPA- $d_8$ . Under the reaction conditions used in this work (140 °C, 5 h and 300 psi of N<sub>2</sub>), no conversion of 2-MF to hydrogenation and ring opening products was observed. The mass fragmentation pattern of 2-MF before reaction (Figure 2.1a, red bars) quantitatively matches that of the NIST database. 82 amu is the parent ion of the undeuterated 2-MF, which is formed by losing one electron in the ionization chamber of the mass spectrometer upon electron impact (Figure 2.2a); therefore, its mass to charge ratio (m/z) equals the molecular mass of 2-MF<sup>66</sup>. The small signal at 83 amu before reaction arises primarily from the natural abundance of <sup>13</sup>C (~1%). Significant

increase in the intensity of the 83 amu signal was observed in the mass fragmentation spectrum of 2-MF after reaction with IPA- $d_8$  (Figure 2.1a and b, blue bars), indicating the incorporation of one deuterium atom.



Figure 2.1. (a) Mass fragmentation pattern of 2-MF before (red bars) and after (blue bars) reaction with IPA- $d_8$  on Ru/RuO<sub>x</sub>/C at 140 °C for 5 h. Inset shows the indices of the carbon atoms in 2-methylfuran. Zoomed-in view of the mass cracking fragment of (b) 80-83 amu, (c) 50-55 amu, (d) 36-42 amu, and (e) 27-32 amu. Insets in (b-e) show the structure of the cracking fragments, and the corresponding indices of the carbons with respect to 2-MF. Mass fragmentation spectra in (b-e) have been rescaled so that the most intense peak is 100 to allow better comparison.

Detailed analysis of other mass fragments of 2-MF before and after reaction suggests that the incorporated D atom is exchanged at the unprotected  $\alpha$ -carbon (C<sub>5</sub>). The mass fragment of 39 amu corresponds to a 3-membered ring cation fragment (Figure 2.1d) containing C<sub>3</sub>, C<sub>4</sub> and C<sub>5</sub> from 2-MF (Figure 2.2a). A significant increase in the signal of 40 amu (+1 amu shift) was observed for the 2-MF after reaction, suggesting that the incorporated D is bonded to one of C<sub>3</sub>, C<sub>4</sub> and C<sub>5</sub> Figure 2.2b). Furthermore, the increase in signal at 30 amu after reaction indicates the incorporation of a D atom in the CHO<sup>+</sup> cation fragment of mass 29 amu (Figure 2.1e), which contains only the  $C_5$  carbon (Figure 2.2a). Thus, analysis of this fragment before and after the reaction indicates that the exchange between H and D occurs in the ring at the C<sub>5</sub> position. The 53 amu signal corresponds to the mass fragment containing  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  (Figure 2.1c), where it is expected that no H/D exchange occurs. However, an increase in the 54 amu signal after reaction is still visible, albeit much less pronounced compared to the previous two cases, suggesting a small degree

exchange exists. This can be rationalized by closely inspecting the mechanism through which the 54 amu fragment is formed 66 (Figure 2.2b, middle pathway). CO, rather than CDO, is lost from the parent ion, and the D originally bonded to  $C_5$ is transferred to C4,

H/D

of



Figure 2.2. Mechanism for the formation of the mass cracking fragments by electron impact (EI) observed in Figure 2.1 for both (a) undeuterated and (b) deuterated (at C5) 2-MF.

which is followed by losing one H (or D) bonded to C<sub>4</sub>. Since the H and D bonded to C<sub>4</sub> are chemically equivalent, the probabilities of losing an H vs. a D are identical. Thus, the probability of forming C<sub>4</sub>H<sub>5</sub><sup>+</sup> and C<sub>4</sub>H<sub>4</sub>D<sup>+</sup> fragments will both be 50% for 2-methylfuran- $d_1$ , resulting in a lower degree of increase of the 54 amu signal than the previous two cases.



Figure 2.3. Quantification of degree of H/D exchange by simulating the mass fragmentation pattern of 2-MF after reaction on Ru/RuO<sub>x</sub>/C at 140 °C for 5 h with a linear combination of the mass fragmentation pattern of 2-MF- $d_0$  and  $d_1$  as in equation (1). Mass fragmentation patterns of (a) 2-MF- $d_0$ , (b) 2-MF- $d_1$ , (c) 2-MF after reaction, and (d) simulated 2-MF.

The degree of H/D exchange in 2-MF after reacting with IPA- $d_8$  can be quantified by decomposing its mass fragmentation pattern of the parent ion cluster into a linear combination of that of 2-MF- $d_0$  and  $-d_1$ , as in equation (2.2):

$$a d_0 + b d_1 = F_{\text{rxn}} \tag{2.2}$$

where both *a* and *b* are weighting coefficients of the clusters  $d_0$  and  $d_1$ , respectively, and  $F_{rxn}$  is the fragmentation pattern of the parent ion cluster after reaction. The weighting coefficients can be computed by using a linear least-squares method to simulate quantitatively the fragmentation pattern of 2-MF formed after the reaction with IPA- $d_8$ . The mass fragment of 2-MF- $d_0$  with an m/z of 81 amu has a sixmembered ring structure (Figure 2.3a), formed by losing one H in the methyl group. Thus, the mass fragment pattern of 2-MF- $d_1$  (D on C<sub>5</sub>) is identical to that of 2-MF- $d_0$  except shifted by +1 amu (Figure 2.3b). The simulated mass fragmentation pattern (Figure 2.3d) matches well with the pattern of 2-MF after H/D exchange reaction, with 17.6% of 2-MF- $d_0$  converted to  $-d_1$  (Table 2.1).

# of Ds added	2-MF	2-EF	2,3-DMF	3-MF	2-MF (red Ru/C)	2-MF (RuO <sub>2</sub> )
+0	83.0±0.8	82.6	49.7	76.0	85.8	94.3
+1	17.0±0.8	17.4	50.3	24.0	14.2	5.7

Table 2.1. Relative percentage of H/D exchange for 2-MF, 2-EF, and 2,3-DMF.

To substantiate the hypothesis that H/D exchange occurs only on the unprotected  $\alpha$ -carbon on the furan ring, reactions were conducted using 2,5-DMF as a reactant with IPA- $d_8$  under identical conditions as those using 2-MF. Since no unprotected  $\alpha$ -carbon in 2,5-DMF exists, no D incorporation is expected. Indeed, no appreciable increase in the 97 amu signal (+1 amu shift from its parent ion of 96 amu)

was observed, confirming the ring activation only occurs on unprotected  $\alpha$ -carbon (Figure 2.4).



Figure 2.4. Mass fragmentation patterns of 2,5-DMF before (red bars) and after (blue bars) reaction with IPA- $d_8$  on Ru/RuO<sub>x</sub>/C at 140 °C for 5h.

Metallic Ru sites are most likely responsible for the H/D exchange activity. This is supported by the reaction of 2-MF and IPA- $d_8$  over reduced Ru/C, where only metallic Ru sites are present. The degrees of H/D exchange on reduced Ru/C and Ru/RuO<sub>x</sub>/C are fairly similar (Figure 2.5b and c), suggesting that the presence of the oxide phase (RuO<sub>x</sub>) does not significantly contribute to the H/D exchange reaction. Only about 6% of 2-MF- $d_0$  was exchanged to  $-d_8$  on RuO<sub>2</sub>. While the literature data suggest that Lewis acids can activate aromatic rings toward hydrogenation,<sup>67-69</sup> the observed exchange activity on RuO<sub>2</sub> does not necessarily prove that the Lewis acid site on RuO<sub>2</sub> can facilitate H/D exchange, because a fraction of RuO<sub>2</sub> is reduced under

the reaction conditions to metallic Ru, which can catalyze the H/D exchange reaction <sup>37,70</sup>. Furthermore, no appreciable amount of H/D exchange occurs on the activated carbon (Figure 2.5a), indicating that the carbon support on the Ru/C catalyst does not play a role in the exchange mechanism.



# 2.5.2 H/D Exchange on other Substituted Furanic Compounds

Figure 2.5. Mass fragmentation patterns of 2-MF before (red bars) and after (blue bars) reaction with IPA- $d_8$  at 140 °C for 5 h on (a) activated carbon, (b) reduced Ru/C, (c) Ru/RuO<sub>x</sub>/C, and (d) RuO<sub>2</sub>. The error bar for relative mass fragment intensity is estimated to be ±1% from several parallel tests.

The presence and nature of substitution group on furan ring play key roles in determining the rates of H/D exchange. To test the generality of the H/D exchange reaction, several furanic compounds without (furan) and with alkyl substitution groups, i.e., 2-ethylfuran (2-EF), 3-methylfuran (3-MF) and 2,3-dimethylfuran (2,3-DMF), were subjected to reaction with IPA- $d_8$  under identical conditions. Unexpectedly, no detectable H/D exchanged in furan (Figure 2.6a) despite having two

unprotected  $\alpha$ -carbons. In contrast, a significant increase in the intensity of the signal at 1 amu higher than the parent ion was observed for all alkyl substituted furans (Figure 2.6b-d), indicating the presence of H/D exchange. The degrees of H/D exchange of different substituted furans are calculated (Table 2.1) following the procedure outlined in Figure 2.3. Approximately 17% of 2-MF and 2-EF are exchanged after reacting with IPA- $d_8$  on Ru/RuO<sub>x</sub>/C at 140 °C for 5 h; whereas about 50% of 2,3-DMF is exchanged under identical conditions. It appears that the presence



Figure 2.6.Mass fragmentation patterns of (a) furan, (b) 2-EF, (c) 2,3-DMF, and (d) 3-MF before (red bars) and after (blue bars) reaction with IPA- $d_8$  at 140 °C for 5 h on Ru/RuO<sub>x</sub>/C.

of alkyl substitutional group promotes the H/D exchange reaction with IPA- $d_8$ .

In addition, the presence of two methyl groups in 2,3-DMF leads to higher degree of H/D exchange than that of 2-MF, 2-EF, and 3-MF. Furthermore, the size of the electron-donating substituent does not appear to play a large role in the exchange, as almost identical percentages of exchange are observed in both 2-MF and 2-EF. 3-MF exhibits higher H/D exchange activity than both 2-MF and 2-EF (~24%), which is likely due to the existence of an additional unprotected  $\alpha$ -carbon. Interestingly, little

H/D exchange was observed for oxygenated furanics, i.e., furfuryl alcohol (FA) and furfural despite having an unprotected  $\alpha$ -carbon. The fragmentation patterns of FA and furfural before and after reaction with IPA- $d_8$  on Ru/RuO<sub>x</sub>/C are almost identical (Figure 2.7). The increases in the signals at 1 amu higher than the parent ion of furan, FA, and furfural are within experimental error, indicating very little or no H/D exchange took place. Computational studies were conducted (in the following section) to understand the differences in the H/D exchange activity of furan with different substitution groups.



Figure 2.7. Mass fragmentation patterns of (a) FA, and (b) furfural before (red bars) and after (blue bars) reaction with IPA- $d_8$  at 140 °C for 5 h on Ru/RuO<sub>x</sub>/C.

#### 2.5.3 Computational Studies on the Reaction Mechanism of H/D Exchange

Our experimental results indicate that the presence of unsubstituted  $\alpha$ carbon(s) is a prerequisite for ring activation of mono or di substituted furans, but unexpectedly, furan itself does not exchange despite having two unprotected  $\alpha$ carbons exposed. Interestingly, ring activation manifests itself only in alkylated furans and the presence of an oxygenated side group prevents ring activation. The dependence on the side group hints at possible electronic effects of substituents on ring activation; however, several convoluted factors, e.g., electronic and solvent effects, could play major roles in metal-mediated ring activation of furans. A Brønsted acid mediated mechanism has been proposed for ring activation in the presence of DCl (deuterated HCl) that entails proton attachment as the slow step followed by ring opening;<sup>71</sup> however, no homogeneous Brønsted acid was introduced to the system. In addition, the possibility of Brønsted acid sites on activated carbon mediating H/D exchange is ruled out by a control experiment using activated carbon, which does not show any detectable level of exchange (Figure 2.5(a)). Furthermore, our calculation suggests that adsorbed H on Ru is negatively charged (Bader charge -0.2), which is unlikely to act as a Brønsted acid site. Therefore, an alternative mechanism must be at play. In order to understand the experimental results, we first performed DFT calculations to map out potential exchange pathways of 2-MF on Ru(0001) at the low coverage limit and in the absence of solvent to identify kinetically feasible pathways and explored solvent effects next.





Figure 2.8. Potential H/D exchange mechanisms in 2-MF. Reaction barriers and reaction energies (in parentheses) for elementary steps at low coverage are given in eV. Values for H/D addition/removal steps are shown in bold.

In Figure 2.8, pathways 1 and 2 correspond to associative and dissociative exchange mechanisms, respectively, analogous to those proposed for ethylene and benzene on Pt and Ni catalysts<sup>72-78</sup>. In mechanism 1, an endothermic D addition with a 1 eV reaction barrier forms an adduct with the C<sub>5</sub>-H bond pointing away from the surface (Figure A.2). Swapping the position of H and D at C<sub>5</sub> is necessary prior to the removal of H, which can potentially occur either via flipping the entire molecule, which is unlikely because the binding energy of this adduct is high (3.3 eV), or via flipping of H and D atoms. An attempt to calculate the barrier for the H/D flipping step resulted in significant deformation of angles at the sp<sup>3</sup> hybridized C atom, followed by rupture of the furan ring. No transition state was identified; breaking the ring occurred with energy penalty > 3 eV. Other orientations of the molecule with the

C-H bond closer to the surface have not resulted in energetically favorable H removal. We conclude that the associative pathway 1 is not likely to occur. The dissociative exchange mechanism 2 entails H removal (endothermic with a moderately high barrier of 0.9 eV) followed by an exothermic D addition. Overall, this path is energetically plausible but is not competitive compared to paths involving ring opening (see below). While the associative/dissociative exchange mechanisms typically involve D addition/H removal in an adsorbed reactant,<sup>72-78</sup> intermediates of 2-MF with higher hydrogenation degree of the ring were also considered, but these paths were deemed unfavorable due to their high endothermicity (>1 eV, data not shown).

Several ring-opening pathways (Figure A.3), including both C<sub>2</sub>-O and C<sub>5</sub>-O scission in 2-MF and its partially hydrogenated derivatives, have also been explored. Formation of ring-open species on metals has been previously demonstrated on  $Pd(111)^{79}$ . No C-C cleavage reactions were considered since they possess high barriers <sup>79</sup>. Mechanisms 3 and 4 (Figure 2.8) entail ring opening at the C<sub>2</sub>-O position with a moderate reaction barrier of 0.5 eV. In pathway 3, D adds to the aldehyde group at C<sub>5</sub> followed by H removal from the same C atom and ring closure, whereas in pathway 4, H removal and D addition steps are swapped. The C-H scission barrier is 1 eV. Mechanism 5 involves ring opening at the C<sub>5</sub>-O position with a barrier of 0.6 eV, followed by D addition and H removal at C<sub>5</sub>; in pathway 6, the latter steps are swapped. Pathways 5 and 6 exhibit the lowest C-H bond breaking/formation barriers of 0.2 and 0.6 eV, respectively, while the D addition barrier in path 5 is 1.1 eV. High ring closure barriers for paths 3-6 (1.1-1.5 eV) are due to the step being highly endothermic (0.6-0.9 eV).

When considering all the above paths in a microkinetic model (not shown) with lateral interactions parameterized (see below), we find that pathway 6 kinetically prevails over all other paths with >99% contribution to the overall H/D exchange rate. To explain the differences in the exchange activity among furans, the elementary reaction energetics for pathway 6 for 2-MF, 3-MF, furan, and FA, was computed (Figure 2.9).



Figure 2.9. Energy diagram for ring-opening pathway 6 (see Figure 2.8 and text) in 2-MF, 3-MF, furan, and furfuryl alcohol on a bare Ru(0001) surface. 2-MF: R<sub>1</sub>=CH<sub>3</sub>, R<sub>2</sub>=H; 3-MF: R<sub>1</sub>=H, R<sub>2</sub>=CH<sub>3</sub>; furan: R<sub>1</sub> =H, R<sub>2</sub>=H; furfuryl alcohol (FA): R<sub>1</sub>=CH<sub>2</sub>OH, R<sub>2</sub>=H. DFT electronic energies for stationary and transition states are reported. Only half of the pathway is shown, with the other half being energetically the same, except for the H atom (orange) substituted by D at the C<sub>5</sub> position.

DFT results indicate that all four reactants share similar energy profiles with energy differences of less than 0.1 eV, except for FA intermediates that are bound 0.6 eV stronger on an average than their MF and furan counterparts. The similarity in energetics can be traced to their very similar binding configurations for the initial, transition and final states (Figure A.4). Different from furan, 2-MF and 3-MF, the OH group of FA intermediates also interacts with the oxophilic Ru surface (Ru-O distance 2.23-2.28 Å), leading to stronger binding. In contrast, the methyl group interacts weakly with the surface due to being farther away, resulting in similar binding energies of furan and alkylated furans.

The electronic effect of ring substituents is unlikely to be the main cause of the differences in H/D exchange activities among furanic molecules. The presence of the CH<sub>3</sub> group in the  $\alpha$  or  $\beta$  position increases the C<sub>5</sub>-O scission barrier slightly (from 0.54 eV in furan to 0.62 eV in 2-MF and 3-MF). In FA, the barrier increases modestly due to the CH<sub>2</sub>OH group (to 0.75 eV). Small but opposite trends are also found for the C<sub>2</sub>-O scission (Table A.2). Similarly, dehydrogenation barriers (0.17-0.19 eV) are independent of the functional group. The ring-opening barrier of furan is 0.08 eV lower than that in 3-MF; however, 3-MF exhibits significantly higher activity in the H/D exchange. Moreover, a more energetically favorable exchange pathway exists in FA that starts with the C<sub>2</sub>-O followed by C<sub>5</sub>-H scission with barriers of 0.38 and 0.31 eV, respectively (Table A.1). Despite the lowest ring-opening barriers among all species, FA does not exhibit any detectable H/D exchange activity rends.

#### 2.5.3.2 Role of Toluene in the Rate of H/D Exchange



Figure 2.10. Furan (b), FA (c), and 3-MF (d) co-adsorbed in 0.75 ML of toluene on Ru(0001). Structure of 1 ML of toluene (a) is shown for comparison. Oblique (6x4) supercell is sketched by the red parallelogram.

In light of the insignificant effect of substitution group on the barriers of H/D exchange, the solvent (toluene) effect on the H/D exchange activity of furanic molecules has also been explored. While no C-H bond activation or H/D exchange is observed for toluene owing to the mild reaction conditions, the presence of toluene affects the adsorption and reaction of co-adsorbed furanic compounds.

The binding energy of toluene is comparable to that of furan compounds (Table A.3), and given that toluene constitutes the greatest fraction of the bulk phase (85 mol.%), we estimated the toluene surface coverage of 0.86 ML at reaction temperature in equilibrium with pure toluene, using the Langmuir isotherm with lateral interactions taken into account. The effect of solvent on adsorption energies can

be significant at such high coverages. In estimating interactions between toluene and intermediates on Ru, we utilize a "monolayer approximation", whereby a relaxed toluene monolayer (an oblique  $(3 \times 2)$  periodic unit cell of toluene molecules (Figure 2.10a)) is considered and one toluene molecule is substituted with an intermediate (in every supercell), as shown in (Figure 2.10b-d). The approach followed here is reminiscent of that introduced by Neurock and co-workers for studying solvent effects.<sup>80</sup> For adsorbed FA and 3-MF, the structures are shown in Figure 2.10c and d. For furan, we considered the orientation (Figure 2.10b) corresponding to the 3-MF conformation, in order to compare the two molecules. 3-MF was selected as the model alkylated furan molecules because it shares the common feature of 2 unprotected  $\alpha$ carbon atoms with furan. The void, visible in Figures 2.10b and 2.10d, is due to the small supercell size used in DFT calculations to minimize computational cost. Calculations for open-ring intermediates as well as for dehydrogenation intermediates were carried out in a similar fashion as in the previous section. Upon ring-opening, only intermediates with the terminal C atom bound to the nearest fcc site were considered.

The presence of toluene has a more pronounced effect on the binding energy of 3-MF than that of furan and FA (Figure 2.11). Co-adsorbed toluene reduces the binding energy of furan by 0.9 eV and of its open ring species even more (1.6-1.8 eV). The effect on the binding of 3-MF exceeds 1.3 eV, becoming greater than 2.2 eV for its open-ring intermediates. The similarity in the binding structure of furan and 3-MF-based species indicates that this weakening in adsorption results from the repulsion between the methyl group and the co-adsorbed toluene. In contrast, the stabilizing interaction of the OH group with the surface for FA is likely to reduce the repulsion

with toluene, leading to a smaller reduction in binding energy (around 1 eV). The importance of solvent on adsorption energies found in our calculations is qualitatively consistent with studies on hydrogenation of phenol in solution.<sup>42</sup> Our calculations and previous literature clearly suggest that solvents can have a profound effect on



Figure 2.11. Change in binding energy of surface intermediates induced by co-adsorbed toluene. R1, R2=H for furan derivatives, R1=H, R2=CH<sub>3</sub> for 3-MF, and R1=CH<sub>2</sub>OH, R2=H for furfuryl alcohol derivatives. Gas phase furan, 3-MF, and furfuryl alcohol, respectively, as well as H adsorbed on 1 ML toluene are used as references.

adsorption energies.

The energy diagram of ring activation in co-adsorbed toluene following path 6 shows that the H/D exchange reaction is significantly more favorable for 3-MF than for furan and FA (Figure 2.12). While on a bare Ru surface 3-MF intermediates are bound 0.1-0.15 eV stronger than those of furan (Figure 2.9), the presence of coadsorbed toluene renders 3-MF intermediates binding 0.2-0.4 eV weaker, i.e., it

changes the relative adsorption strength. FA exhibits the strongest binding in both without and with co-adsorbed toluene. This solvent-induced change in binding energies has significant ramifications for the kinetics of H/D exchange, as illustrated



Figure 2.12. Energy diagram for H/D exchange pathway with co-adsorbed toluene (0.75 ML).

microkinetic modeling below.

by

Microkinetic model with toluene coverage effects taken into account (Figure A.1) reproduces similar experimental trend for the H/D exchange rates in 3-MF, 2-MF, furan, and FA (relative rates 1.0, 1.1,  $\sim 10^{-8}$ , and  $\sim 10^{-12}$ , respectively). The effect of solvent on the H/D exchange activity becomes apparent in the coverage of vacancies and C-containing species shown in Figure 2.13 (balance is toluene; coverage of IPA derivatives is negligible). For 3-MF and 2-MF, the coverage of C-containing species is low and the fraction of vacancies is higher due to their weaker

binding caused by the repulsion of  $CH_3$  with toluene (Figure 2.12). In contrast, furan and FA block the catalyst sites more effectively due to lack of steric effects with toluene in the former case and the interaction of oxygen of -CH<sub>2</sub>OH with Ru in the



Figure 2.13. Simulated surface coverages for vacant sites and C-containing intermediates at the end of 5-hour period. The balance is adsorbed toluene. Temperature 140 °C, initial mixture containing 2 mol. % of oxygenate, 13 mol. % of IPA-d<sub>8</sub>, and 83 mol. % of toluene.

latter case.

Sensitivity analysis suggests that IPA- $d_8$  dehydrogenation to form deuterated propoxy and adsorbed deuterium is a kinetically important reaction step for all reactants (Figure 2.14), which is likely to be a consequence of a relatively high reaction barrier (0.8 eV; Table A.1). For 2-MF and 3-MF, O-D scission in IPA is the most kinetically important step, indicating that the H/D exchange rate is dictated by deuterium production rate in the system. For furan and FA, on the other hand, adsorption and desorption steps become kinetically relevant. This is in line with stronger binding of furan and FA intermediates (Figure 2.12), leading to higher blocking of sites and limiting the overall H/D exchange rate. Clearly, the solvent plays a key role in adsorption and rendering these kinetically relevant steps. In light of surface blocking, a similar effect has been proposed to explain the lack of H/D



Figure 2.14. Normalized sensitivity coefficients for five types of reactions in the H/D exchange mechanism 6. Reaction barriers were perturbed by 0.13 eV.

exchange in thiophene on reduced transition metal surfaces.<sup>81</sup>

The combination of experimental and computational investigation of the solvent effect on H/D exchange activity on Ru-based catalysts suggests that the relative strength of adsorption of reactants, intermediates and solvents could play a decisive role in the reaction rates and product distribution. This fundamental understanding could be used to explain the lack of H/D exchange of furfural (Figure

2.7), because the adsorption energy of furfural on Ru(0001) (-2.49 eV) is comparable to that of FA (-2.42 eV) (Table A.3), with the corresponding ring-opening intermediates bound even more strongly (<-2.9 eV). In addition, it opens up the possibility of computational screening of solvents based on relative adsorption energy of reactants, intermediates and solvents on the surface of catalysts. The proposed ringopening mechanism for H/D exchange could shed light on molecular-level understanding of ring opening reactions for furanic compounds on Ru-based surfaces, which is an important family of reactions for production of renewable diols, alkanes, and alkenes <sup>40,82,83</sup>. The metal mediated activation of aromatic ring is likely to be the first step in the ring opening reactions for furanic compounds, followed by further hydrogenation and hydrogenolysis steps. The mechanistic insights gained in this work show that the facile formation of strongly bound species with broken furan ring may result in partial blocking of catalytic sites, inhibiting kinetics of subsequent reactions, such as hydrodeoxygenation. Thus, tuning the strength of adsorption of the ring opened intermediates on the catalyst surface could be a key factor in efficiently catalyzing ring opening reactions.

# 2.6 Conclusions

We demonstrate via a combination of isotopic labeling experiments, DFT calculations, and first-principles microkinetic modeling that the H/D exchange of alkylated furans occurs through a Ru surface mediated ring-opening pathway. Detailed mass fragmentation pattern analysis shows that only alkylated furans with unprotected  $\alpha$ -carbons exhibit appreciable H/D exchange activity; in contrast, furan, furfuryl alcohol, and furfural do not exhibit noticeable H/D exchange. Our results are in sharp contrast with Brønsted acid catalyzed ring activation where proton transfer to the  $\beta$ 

carbon of the ring is kinetically relevant and precedes ring opening.<sup>71,84</sup> DFT calculations and microkinetic modeling with co-adsorbed toluene (solvent) suggest the most likely pathway involves Ru-surface mediated scission of the C-O bond in the furan ring at the unsubstituted carbon atom, followed by dehydrogenation, deuteration, and ring closure steps. This mechanism provides qualitative agreement with the experiment (quantitative agreement is impossible due to approximations inherent to semilocal DFT and the mean-field microkinetic model). Unexpectedly, the degree of H/D exchange reaction depends on the adsorption strength of exchange intermediates: The latter is governed from the interaction of the substituent group both with the surface and with co-adsorbed solvent molecules. The adsorption energy of alkylated furans, such as in 2-MF and 3-MF, is significantly weakened by the repulsive interaction between the alkyl groups on the furan ring and co-adsorbed toluene (solvent), as compared to furan. In contrast, furanic compounds with oxygen containing functional group interact strongly with the Ru surface, and this interaction more than offsets its repulsive interaction with co-adsorbed toluene. As a result, strongly bound compounds, e.g., furan and furfuryl alcohol derivatives, inhibit H/D exchange mainly by site blocking and slow desorption. Our results expose a rather unexplored mechanism of solvent effects. This molecular level understanding of the solvent effect on the activity could guide the choice of solvents for a broad range of other reactions. Furthermore, the proposed furan ring-opening pathway for the H/D exchange is likely the initial step towards the formation of ring opening products, such as alkanes for fuels and 1,6 hexanediol and adipic acid for renewable monomers.

# Chapter 3

# CONJUGATION-DRIVEN "REVERSE MARS-VAN KREVELEN"-TYPE RADICAL MECHANISM FOR LOW TEMPERATURE C-O BOND ACTIVATION

## 3.1 Abstract

C-O bond activation on monofunctional catalysts (metals, carbides, and oxides) is challenging due to activity constraints imposed by energy scaling relationships. Yet, contrary to predictions, recently discovered multifunctional metal/metal oxide catalysts (e.g., Rh/ReO<sub>x</sub>, Rh/MoO<sub>x</sub>, Ir/VO<sub>x</sub>) demonstrate unusually high C-O scission activity at moderate temperatures. Herein, we use extensive density functional theory calculations, first principles microkinetic modeling, and electronic structure analysis to elucidate the metal/metal oxide synergy in the Ru/RuO<sub>2</sub> catalyst, which enables up to 76% yield of the C-O scission product (2-methyl furan) in catalytic transfer hydrogenolysis of furfural at low temperatures. Our key mechanistic finding is a facile radical-mediated C-O bond activation on RuO<sub>2</sub> oxygen vacancies, which directly leads to a weakly bound final product. This is the first time the radical *reduction* mechanism is reported in heterogeneous catalysis at temperatures <200°C. We attribute the unique catalytic properties to the formation of a conjugationstabilized furfuryl radical upon C-O bond scission, the strong hydroxyl affinity of oxygen vacancies due to the metallic character of RuO<sub>2</sub>, and the acid-base heterogeneity of the oxide surface. The conjugation-driven radical-assisted C-O bond scission applies to any catalytic surface that preserves the  $\pi$ -electron system of the

reactant and leads to C-O selectivity enhancement, with notable examples including Cu, H-covered Pd, self-assembled monolayers on Pd, and oxygen covered Mo<sub>2</sub>C. Furthermore, we reveal the cooperativity of active sites in these multifunctional catalysts. The mechanism is fully consistent with kinetic studies and isotopic labeling experiments, and the insights gained might prove useful more broadly in overcoming activity constraints induced by energy scaling relationships.

#### 3.2 Introduction

Selective C-O bond scission is essential in various industrially important chemical processes. For example, in Fischer-Tropsch synthesis, which experiences revival due to the revolution of shale gas<sup>85</sup>, C-O bond activation can potentially govern the hydrocarbons-to-alcohols product ratio<sup>86,87</sup>. Selective C-O cleavage is also crucial in the first-generation biofuels production, as it is implicated in the conversion of glycerol byproduct to the commodity chemical propylene glycol<sup>88</sup>. For emerging second-generation biofuels and chemicals, efficient oxygen removal is necessary for integration into the downstream oil refining infrastructure<sup>89</sup>.

Unlike reforming and dehydrogenation, which involve C-C and C-H bond breaking, the design of a selective C-O scission catalyst represents a significant challenge. Activity and selectivity maps for small oxygenates, such as ethylene glycol, indicate that the best deoxygenation metal catalysts would be orders of magnitude slower than good reforming catalysts at the same reaction conditions<sup>90,91</sup>. Experimental studies of ethanol conversion on group 8-11 transition metal catalysts of varying oxophilicity (Cu, Pt, Pd, Ir, Rh, Ru) confirm that reforming reactions are dominant and the yield to hydrocarbons (ethylene and ethane) is negligible<sup>92</sup>. Similarly, UHV experiments indicate that the rates of 1-propanol and ethylene glycol selective deoxygenation on oxophilic  $Mo(110)^{93}$  and  $Mo_2C^{94}$  surfaces are lower than that of C-C bond scission over reforming catalysts Ni(111) and Fe/Ni(111)<sup>95</sup>. Late transition metals are deemed ineffective for C-O scission due to poisoning by the CO by-product and requirement of large metal clusters<sup>96</sup>.

An alternative strategy for C-O bond activation utilizes reducible transition metal oxides. In the "reverse Mars van Krevelen<sup>97</sup> mechanism", an oxide surface is being reduced by hydrogen to produce oxygen vacancies, which in turn abstract oxygen atoms from O-containing reactants, restoring the initial surface structure. Roman-Leshkov and co-workers<sup>98-100</sup> found MoO<sub>3</sub> to be efficient for deoxygenation of ketones, furanics, and aromatics at low H<sub>2</sub> pressures with up to 98% selectivities. However, a temperature of 320 °C was required for the oxide to acquire sufficient deoxygenation activity. Similarly, oxygen vacancies of CeO<sub>2</sub>-ZrO<sub>2</sub> were active for guaiacol conversion above 325-350 °C<sup>101</sup>, and WO<sub>3</sub> bronzes were active for hydrodeoxygenation of acrolein above 300-350 °C<sup>102</sup>. There is a clear need for more active, low temperature C-O bond activation catalysts.

Over the last few years, a plethora of transition metal/metal-oxide hybrid catalysts (TM/MO) has been developed, which, unlike metals and oxides alone, are capable of selectively and effectively catalyzing C-O bond scission at moderate temperatures (100-200 °C). Examples include glycerol hydrogenolysis to either 1,2-propanediol on Ru/ReO<sub>x</sub><sup>103</sup> and Rh/ReO<sub>x</sub><sup>104</sup> or 1,3-propanediol on Ir/ReO<sub>x</sub><sup>105</sup>, ring opening in tetrahydrofurfuryl alcohol on Ir/VO<sub>x</sub><sup>106</sup>, ring opening in tetrahydropyran-2-methanol on Rh-ReO<sub>x</sub> to form 1,6-hexanediol<sup>107</sup>, and deoxygenation and ring-opening reactions in diols, triols, furans, and pyrans on Rh-ReO<sub>x</sub> and Rh-MoO<sub>x</sub><sup>108</sup>.

The high C-O scission activity over many TM/MO catalysts for chemically and structurally different reactants hints to a potentially general C-O bond activation mechanism that remains poorly understood and occasionally controversial. Chia et al. proposed a Brønsted acid-catalyzed mechanism via oxocarbenium ions involving OH groups on Re single atoms incorporated into the Rh surface, based on NH<sub>3</sub> temperature-programmed desorption experiments and DFT calculations<sup>108</sup>. The proposed C-O bond scission with simultaneous hydride transfer from  $\alpha$ -C to  $\beta$ -C as the rate-limiting step is in variance with a first-order reaction with respect to hydrogen and the observed deuterium incorporation at the  $\beta$ -C position in isotopic labeling experiments, carried out by Tomishige and co-workers for tetrahydrofurfuryl alcohol ring-opening<sup>109</sup>. Instead, a direct hydride attack mechanism occurring on the Rh (or Ir)/ReO<sub>x</sub> interface was proposed. In the hydrodeoxygenation of furfuryl alcohol on Ru/RuO<sub>2</sub>, isotopic labeling experiments<sup>110</sup> indicated oxygen removal with

simultaneous furan ring activation by hydrogen. DFT calculations<sup>4</sup> clearly showed that RuO<sub>2</sub> Lewis acid sites are inefficient for C-O bond hydrogenolysis,



**Scheme 1.** Catalytic transfer hydrogenolysis (CTH) of furfural (FAL) to form 2-methyl furan (2-MF) using 2-propanol as a hydrogen donor. The latter is converted to acetone.

but the active site and the role of Ru remained elusive.

In order to elucidate the TM/MO oxide synergy for C-O bond activation, here we investigate a model reaction system, namely the catalytic transfer hydrogenolysis (CTH) of furfural (FAL) to yield 2-methylfuran (2-MF) on the Ru/RuO<sub>2</sub> catalyst, using 2-propanol as a solvent and hydrogen donor (Scheme 1). 2-MF yields of 76% at

moderate temperatures (<200 °C) in the liquid phase<sup>37,111</sup>, unattainable on Ru and RuO<sub>2</sub> catalysts alone, were reported. 2-MF can be a renewable drop-in fuel or converted to jet fuels, lubricants<sup>24</sup>, and aromatics<sup>112,113</sup>; furfural is produced industrially from lignocellulosic biomass. We find a rather unexpected radical reverse Mars van Krevelen-type mechanism over metal oxide vacancies that rationalize the high C-O bond hydrogenolysis activity. We show that a radical intermediate is a prerequisite for the facile C-O scission reaction and this finding is consistent with the deuterium distribution in H/D labeling experiments and reactivities of aromatic vs. aliphatic oxygenates. To the best of our knowledge, this is the first evidence for a radical *reduction* mechanism (as opposed to radical oxidation) in heterogeneous catalysis being operative at temperatures below 200-250 °C. We elucidate a rather complex, trifunctional behavior of a TM/MO catalyst: Lewis acid sites of RuO<sub>2</sub> convert furfural to furfuryl alcohol via the Meerwein-Ponndorf-Verley (MPV) mechanism; oxygen vacancies catalyze C-O bond hydrogenolysis; and metallic sites provide hydrogen for vacancy formation. High reaction rates, e.g., in C-O scission, can be linked to moderate oxophilicity of metallic or oxide surfaces via universal linear scaling relationships <sup>114-117</sup>. While RuO<sub>2</sub> vacancies exhibit lower O binding energy than metallic Ru(0001) sites, we find that the former are much more catalytically active in C-O scission and water formation. We attribute this counterintuitive catalyst behavior to a conjugation-stabilized radical intermediate, unusually strong hydroxyl affinity of oxygen vacancies due to the metallic character of RuO<sub>2</sub>, and acid-base heterogeneity of the RuO<sub>2</sub> surface.

# 3.3 Methodology

### **3.3.1 Density Functional Theory (DFT) Calculations**

Reaction energetics on Ru(0001) and  $RuO_2(110)$  model catalytic surfaces were calculated using the DFT Vienna ab initio simulation package (VASP) code, version 5.3.3<sup>43-46</sup>. The Ru(0001) surface was modeled as a four-layer  $p(4 \times 4)$  slab with two bottom layers fixed in their bulk positions. The  $RuO_2(110)$  surface has been cleaved along the (110) crystal plane, which is known to possess the lowest surface energy<sup>118</sup> and has been observed experimentally<sup>119,120</sup>. We employed the  $p(3\times 2)$  supercell with four O-Ru-O stoichiometric trilayers along the z-direction. Three top atomic layers (O-Ru-O) were allowed to relax during optimization of ionic degrees of freedom, with the remaining atoms held fixed. Since ruthenium oxide (IV) belongs to a class of metallic oxides with substantial electron delocalization and no band  $gap^{121}$ , reasonable performance of the GGA approximation can be expected. In this work, we use the exchange-correlation functional by Perdew. Burke, and Ernzerhof (PBE)<sup>14</sup> for both Ru and RuO<sub>2</sub> surfaces, which has been shown to yield an accurate RuO<sub>2</sub> electronic structure<sup>122</sup> and RuO<sub>2</sub>(110) reaction energetics in agreement with experimental data<sup>123</sup>. Grimme's dispersion correction, D3<sup>49</sup>, has been added to account for non-covalent interactions of the furan ring with the surface. Further computational details and benchmarking of vacancy formation energetics are reported in Section B.1.

## 3.3.2 First Principles-based Microkinetic Model

Microkinetic models for vacancy formation under ultra-high vacuum conditions and furfuryl alcohol hydrogenolysis on RuO<sub>2</sub> in a liquid phase environment of a batch reactor were set up using an in-house Fortran code built around CHEMKIN<sup>TM63,64</sup>. Lists of elementary reactions, reaction conditions, calculations of

reaction orders and the apparent activation energy, and all simulation details can be found in Sections B.3 and B.4.

### **3.4** C-O Bond Hydrogenolysis on Ru(0001) and RuO<sub>2</sub>(110)

We first explore furfural hydrogenation to furfuryl alcohol on Ru and RuO<sub>2</sub>; both materials are effective in catalyzing furfural hydrogenation albeit via a different mechanism (see Figure B.1). The metal follows a Horiuti-Polanyi-type sequential endothermic addition of co-adsorbed hydrogen atoms to the C=O bond starting with C-H and followed by O-H bond formation, with the highest barrier of 1.0 eV in the latter step (Table B.1, Figure B.2). The oxide carries out direct intermolecular hydride transfer from 2-propanol to furfural via the MPV mechanism on Lewis acid sites<sup>4</sup>. The barrier in the MPV mechanism is only 0.2 eV, indicating the RuO<sub>2</sub> is more efficient than Ru in C=O hydrogenation, consistent with isotopic tracing experiments and a kinetic isotope effect<sup>110</sup>.

Next, we turn to the hydrogenolysis reaction. Reaction pathway energetics for subsequent transformation of furfuryl alcohol to 2-MF on Ru(0001) and RuO<sub>2</sub>(110)<sup>4</sup> surfaces are shown in Figure 3.1 (see Figure B.2 and Table B.1 for structures and energetics). On both surfaces, strongly adsorbed FCH<sub>2</sub>OH (binding energies -2.5 and - 1.8 eV, respectively) undergoes a facile O-H bond scission yielding a furoxy species, FCH<sub>2</sub>O. The following C-O bond breaking on Ru(0001) is facile with a 0.7 eV barrier, and the resulting furfuryl species FCH<sub>2</sub> easily reacts with a hydrogen atom to form 2-MF that desorbs from the surface. The hydrogenolysis efficiency of the Ru(0001) surface is overshadowed by the difficulty of hydrogenating the produced surface oxygen atoms and complete the catalytic cycle, as the barriers for adding the first and second hydrogen atom to form water are 1.6 and 1.3 eV, respectively. The difficulty of



Figure 3.1. Minimum energy DFT reaction pathways for furfuryl alcohol conversion to 2-methyl furan (2-MF) on Ru(0001) (black) and RuO<sub>2</sub>(110) (red) surfaces. All energies are referenced to furfuryl alcohol and H<sub>2</sub> in vacuum and bare Ru(0001) and RuO<sub>2</sub>(110) slabs. F denotes the furan ring with H at C<sub>1</sub> position removed (C<sub>4</sub>H<sub>3</sub>); O, H, OH, and H<sub>2</sub>O refer to the corresponding chemisorbed species. Data for RuO<sub>2</sub> are taken from<sup>4</sup>.

removing oxygen from Ru surfaces below the 0.25 ML coverage is well known in surface science studies<sup>124,125</sup> and lies in the high oxophilicity of metallic Ru. Our microkinetic modeling indicates that the oxygen coverage is high (not shown); DFT calculations indicate that 0.25 ML O/Ru(0001) with a p(2x2) periodicity increases the C-O scission barrier in furoxy species by at least 0.8 eV compared to bare Ru (Table B.1). On more open Ru nanoparticle facets and edges, the inhibition by surface oxygen is likely to be even more prominent due to lower metal coordination numbers<sup>126,127</sup>. In summary, the high oxophilicity of Ru, which leads to facile C-O bond scission, is also responsible for the slow formation of water and an increase in

the deoxygenation barriers at higher oxygen coverages, leading to modest catalyst activity.

On  $RuO_2(110)$ , on the other hand, the C-O scission barrier in FCH<sub>2</sub>O over Ru<sub>cus</sub> Lewis acid sites (see Scheme 2) is prohibitively high  $(1.9 \text{ eV})^4$ , rendering the RuO<sub>2</sub> phase inefficient for activating C-O bonds. In addition, the RuO<sub>2</sub> surface binds water molecules strongly (1.4 eV desorption barrier). The above findings clearly show that neither Ru nor RuO<sub>2</sub> are active catalysts for hydrogenolysis in with agreement



Scheme 2. Top two O-Ru-O layers of a  $RuO_2(110)$  surface. Bridging oxygen (O<sub>br</sub>), coordinatively unsaturated Ru sites (Ru<sub>cus</sub>), and oxygen vacancies are shown.

experiments<sup>37,120</sup>, and raise the question of which is the active site and the mechanism in these systems.

### 3.5 C-O Bond Hydrogenolysis Active Site

XANES/EXAFS results reveal that RuO<sub>2</sub> is being reduced to metallic Ru over the course of catalytic transfer hydrogenolysis<sup>120</sup>. Scanning tunneling microscopy (STM) experiments have shown<sup>128,129</sup> that RuO<sub>2</sub> reduction commences with formation of metallic Ru nanoclusters and patches on the oxide surface. Patches of one metal on the other are known to greatly enhance catalyst activity by coupling two different catalyst functionalities via surface spillover, e.g., in ammonia decomposition<sup>130</sup>. In the Ru/RuO<sub>2</sub> system, Ru is active in C-O bond breaking, and RuO<sub>2</sub> is effective in oxygen removal; however, due to large difference in oxygen binding energies (-0.5 vs. +0.8 eV on Ru(0001) and RuO<sub>2</sub> (110), respectively; Table B.2), oxygen spillover is unlikely. Metal-metal oxide synergy has also been attributed to interfacial sites, for example, in CO oxidation on Au/TiO<sub>2</sub> <sup>131</sup>. Our detailed calculations rule out this possibility as well. We found that the Ru/RuO<sub>2</sub> interface does not considerably enhance the Lewis acid oxophilicity; also, metallic Ru becomes even more oxophilic, exacerbating oxygen poisoning (Section B.2). Consequently, the direct contact between Ru and RuO<sub>2</sub> phases is not advantageous for efficient C-O bond hydrogenolysis. A Brønsted acid-catalyzed mechanism is also thermodynamically unfavorable (Table B.6, reaction 16). Our findings refute most common synergy mechanisms on metal/metal oxide catalysts.

Oxygen vacancies play a vital role in a plethora of metal oxide-catalyzed chemical processes, such as methane oxidation on  $PdO_x/ZrO_2^{132}$ , CO oxidation on Auand ZrO<sub>2</sub>- promoted CeO<sub>2</sub><sup>133,134</sup>, RuO<sub>2</sub><sup>119</sup>, and Pt<sub>1</sub>/FeO<sub>x</sub><sup>135</sup>, or propene oxidation on bismuth molybdates<sup>136</sup>. RuO<sub>2</sub>(110) forms vacancies already at room temperature upon H<sub>2</sub> exposure<sup>137</sup>. This motivated us to consider oxygen vacancies as a possible active site for low temperature C-O bond hydrogenolysis.

The minimum energy pathway for furfuryl alcohol conversion to 2-MF over an oxygen vacancy is shown in Figure 3.2 (states A-D). Due to the extremely high affinity of  $O_{br}$  surface sites toward hydrogen (-3.8 eV H binding energy vs. -2.7 to -3 eV on group 8-10 transition metals<sup>138</sup>), all  $O_{br}$  are capped by hydrogen atoms via a low-barrier (<0.5 eV), highly exothermic hydrogen abstraction from the 2-propanol solvent (Table B.6). Furfuryl alcohol chemisorption occurs via the OH group to the vacancy in a mildly exothermic step (binding energy -0.8 eV). Positive total Bader charge of the alcohol molecule (+0.09) reveals minor electron donation to the surface, indicating that the vacancy acts as a Lewis acid, similar to neighboring Ru<sub>cus</sub> sites (see

Table B.7). The subsequent C-OH scission is highly favorable with a reaction barrier of 0.3 eV. The leaving OH group annihilates the oxygen vacancy, leaving behind a weakly adsorbed furfuryl fragment FCH<sub>2</sub> (-0.3 eV binding energy). Followed by OH group rotation with a barrier of ~0.3 eV (state B-C), the furfuryl fragment reacts with surface hydroxyl (0.1 eV barrier), resulting in a physisorbed final product – 2-MF (-0.4 eV binding energy). The reaction can proceed in a single concerted step or may involve migration of the weakly bound furfuryl fragment to neighboring hydroxyls. Favorable reaction energetics makes it clear that oxygen vacancies are by far the most active sites in deoxygenation.

Even more interestingly, the spin electron density plotted for state B (inset of Figure 3.2) displays localization of an unpaired electron on a furfuryl fragment at C<sub>1</sub>, C<sub>3</sub>, and C<sub>5</sub> positions, indicating the formation of a furfuryl radical intermediate over the course of the reaction. Radical intermediates on oxide surfaces are ubiquitous in catalytic oxidation of alkanes and alkenes<sup>139-143</sup>; yet this chemistry frequently involves C-H scission barriers >1 eV and thus requires high temperatures (>300 °C) in order to achieve appreciable reaction rates. The low barrier in the C-OH scission signifies that radicals can also mediate heterogeneous catalytic processes involving reduction, potentially at much lower temperatures (<200 °C). However, the feasibility of the radical reduction mechanism depends on the catalyst effectiveness and its ability to complete the catalytic cycle. This is discussed next.


Figure 3.2. Minimum energy reaction pathway for C-OH bond scission in furfuryl alcohol, adsorbed over a vacancy on a hydroxylated RuO<sub>2</sub>(110) surface, along with associated structures. One possibility for H abstraction by a furfuryl radical is shown; due to its weak interaction with the surface, furfuryl can migrate along the surface and react with more remote hydroxyls. The inset depicts unpaired electron density (spin  $\frac{1}{2}$  minus spin  $-\frac{1}{2}$ ) for state B. Purple denotes areas with dominant localization of S =  $-\frac{1}{2}$  electrons; green – with S =  $\frac{1}{2}$  electrons. Bader sphere-projected atomic spin densities on C<sub>1</sub>, C<sub>3</sub>, and C<sub>5</sub> atoms are 0.41, 0.23, and 0.21 Bohr-magnetons, respectively.

#### **3.6** Vacancy Formation Mechanism on RuO<sub>2</sub>(110)

The vacancy-mediated C-O bond hydrogenolysis demands continuous *in situ* regeneration of the catalytic sites and a key step in this cycle is vacancy formation. Vacancy formation has been suggested to occur via the removal of the bridging O<sub>br</sub>H

group by a neighboring H atom adsorbed on a Ru<sub>cus</sub> site, forming a H<sub>2</sub>O molecule on Ru<sub>cus</sub><sup>137</sup>. Our DFT calculations could not identify a transition state with < 2 eV reaction barrier; difficulty of removing O<sub>br</sub>H is likely due to its strong binding to the surface (-4.0 eV binding energy over a vacancy). Vacancy formation from two neighboring O<sub>br</sub>H groups, suggested for TiO<sub>2</sub> (110)<sup>144</sup>, is also unfavorable (Table B.6, reaction 4). It is clear that the typically postulated mechanisms for vacancy formation are ineffective.

In order to elucidate the mechanism, consistent with vacancy formation at room temperature, we investigated computationally several possible ways a hydrogen molecule can react with a non-hydroxylated<sup>4</sup> and a hydroxylated  $RuO_2(110)$  surface (Table B.6), leading to vacancy formation. The microkinetic model (Section B.3), containing all such reactions, reproduces well all essential features observed upon 100 Langmuir H<sub>2</sub> exposure at 25 °C using STM/x-ray photoelectron spectroscopy (XPS). In particular, we find OH<sub>br</sub> hydroxyls to be dominant on the surface; transformation of ~5% O<sub>br</sub> to vacancies; and formation of water molecules on Ru<sub>cus</sub> sites (Table B.8). The model also reproduces an experimental two-peak temperature programmed desorption/reduction  $H_2O$  profile quite well (Figure B.5). Reaction path analysis reveals a rather novel, low temperature vacancy formation mechanism that begins with associative adsorption of H<sub>2</sub> on Ru<sub>cus</sub> of a hydroxylated surface (-0.5 eV binding energy), followed by a slightly endothermic ( $\Delta E = +0.2 \text{ eV}$ ), low barrier (0.4 eV), heterolytic H<sub>2</sub> splitting to form co-adsorbed H on Ru<sub>cus</sub> and H<sub>2</sub>O<sub>br</sub> water-like species (Figure 3.3). H can subsequently react with OH<sub>br</sub> to form H<sub>2</sub>O<sub>br</sub>. Unlike O<sub>br</sub> and O<sub>br</sub>H, H<sub>2</sub>O<sub>br</sub> is weakly bound to the surface (-0.6 eV binding energy), and thus can either desorb as water or migrate to a proximal vacant Ru<sub>cus</sub> site (0.4 eV barrier, -0.6 eV

exothermic), resulting in vacancy formation in both scenarios. The microkinetic model indicates that the surface coverage of  $H_2O_{br}$  never exceeds  $10^{-11}$  ML (a reactive precursor) and rationalizes the lack of observing it in STM and XPS studies, which led to the postulate that this is not an important precursor<sup>137,145</sup>. Taken together, DFT and microkinetic simulation provide strong evidence for a vacancy formation mechanism with the  $H_2O_{br}$  species as a vacancy precursor.



Figure 3.3. Vacancy formation mechanism, as determined by the reaction path analysis in the microkinetic model. Reaction barriers (reaction energies) in eV.

# 3.7 Multi-functional Catalytic Mechanism

One important question is how the hydrogen donor forms the  $H_2O_{br}$  species. We believe that there are two important contributions. First, 2-propanol can easily form a fully hydroxylated surface, with all  $O_{br}$  capped with H. Upon hydroxylation, the  $OH_{br}$  is no longer able to dehydrogenate alcohol: final states for sequential C-H/O-H scission cannot be identified using DFT, whereas the simultaneous C-H/O-H bond scission is 1.2 eV endothermic. Second, small amounts of hydrogen, produced *in situ* during CTH hydrogenolysis on metallic Ru from dehydrogenation of 2-propanol<sup>5,146</sup> (due to ineffectiveness of the hydroxylated RuO<sub>2</sub>), generate vacancies as discussed above, which catalyze the hydrogenolysis of furfuryl alcohol, completing the catalytic cycle (Figure 3.4a). While the metallic Ru surface can partially be oxidized due to high reaction barriers for removal of surface oxygen (Figure 3.1), at the 0.25 ML O/Ru(0001) coverage, the C-O bond scission is inhibited (Table B.1, reactions 10-11), preventing further surface oxidation and making metallic Ru sites available for H<sub>2</sub> production. In contrast, C-H and O-H bond scission reactions, involved, for example, in 2-propanol dehydrogenation, can still proceed on the 0.25 ML O/Ru(0001) surface<sup>147</sup>.

Starting with furfural as a reactant, Ru/RuO<sub>2</sub> exposes trifunctional catalysis: furfural is converted to furfuryl alcohol on Ru<sub>cus</sub> Lewis acidic sites of RuO<sub>2</sub> via the MPV mechanism<sup>110</sup>; furfuryl alcohol undergoes C-OH scission on RuO<sub>2</sub> oxygen vacancies, forming 2-MF and oxidizing the vacancy; and finally, H<sub>2</sub> is produced on metallic Ru sites via dehydrogenation of the hydrogen donor. H<sub>2</sub> in turn regenerates vacancies and closes the catalytic cycle (Figure 3.4b). The highest reaction barrier on each of three catalytic sites is lower than 0.9 eV, rendering the reaction mechanism feasible at moderate reaction temperatures < 200°C. An advantage of having a hydrogen donor, instead of external hydrogen, is that it enables selective carbonyl group hydrogenation via the MPV scheme, and the small amount of H<sub>2</sub>, generated over the course of the reaction, prevents rapid reduction of the oxide catalyst, which will render the catalyst ineffective.



Figure 3.4. (a) Mars-van Krevelen-type reaction mechanism of furfuryl alcohol hydrogenolysis over oxygen vacancies of  $RuO_2(110)$  surface. DFT-based reaction barriers (energies) in eV. Associative adsorption steps are assumed to be non-activated. Desorption barriers are taken as equal to absolute values of species binding energies. Two variants of the vacancy formation mechanism (involving H<sub>cus</sub> or H<sub>2cus</sub>; Figure 3.3) and H abstraction from 2-propanol/propoxy by O<sub>br</sub> are shown in an abbreviated form. (b) Synergy of Ru and RuO<sub>2</sub> active sites for hydrogenolysis of furfural. Numbers indicate the highest reaction barrier (in eV) for each cycle. The barrier over  $Ru_{cus}$  (Lewis acid sites) is taken from<sup>4</sup>; the dehydrogenation barrier over metallic Ru is taken from<sup>5</sup>.

Microkinetic model for furfuryl alcohol hydrogenolysis (Section B.4) reproduces well an experimental second order rate constant  $(0.016 \text{ L} \text{ mol}^{-1} \text{ h}^{-1})^{110}$ , if the ratio between Ru and RuO<sub>2</sub> catalytic surface areas is ~  $3 \cdot 10^{-4}$ , consistent with the fresh catalyst predominantly composed of RuO<sub>2</sub>. Sensitivity analysis (Table B.9) reveals the overall hydrogenolysis rate to be governed by hydrogen generation from 2-propanol on metallic Ru sites. 2-propanol dehydrogenation as a rate-limiting step conforms to an experimentally observed effect of hydrogen donor dehydrogenation activity on the hydrogenolysis rate<sup>111</sup> and is consistent with the kinetic isotope effect upon replacement of hydrogen donor with its fully deuterated counterpart<sup>110</sup>.

Deuterated 2-propanol leads to incorporation of deuterium in both  $C_1$  (methyl group) and  $C_3$  (furanic ring) positions of 2-MF.<sup>110</sup> The reasons for such incorporation have though remained elusive. The inset of Figure 3.2 shows that the furfuryl radical intermediate possesses an unpaired electron delocalized between  $C_1$ ,  $C_3$ , and  $C_5$ . Consequently, both  $C_1$  and  $C_3$  are susceptible to the D attack, whereas the  $C_5$  atom is likely distant from the surface, particularly in a crowded surface environment of a liquid phase reaction. D addition to  $C_3$  has a negligible barrier (0.07 eV) and is



Figure 3.5. Mechanism of deuterium incorporation at  $C_1$  and  $C_3$  positions of 2-MF. Numbers in parentheses indicate DFT reaction barriers (energies) in eV.

isoenergetic (+0.01 eV; Figure 3.5). We included the corresponding D addition/H removal steps into a microkinetic model (Section B.4) and simulated massspectrometric peaks, with results shown in Figure 3.6. The first principles model quantitatively predicts D incorporation into the ring of ~40% of 2-MF molecules. M/z=82 and m/z=85 amu peaks demonstrate excellent agreement with the experiment. Underestimation of the m/z=83 amu peak is likely caused by the not-accounted reaction FCHDOD+2H → FCH<sub>2</sub>D+DHO due to the presence of a mobile protium source in the system, e.g., OH<sub>br</sub> groups on a fresh RuO<sub>2</sub> catalyst surface. When FCH<sub>2</sub>OH containing mobile hydroxyl protium is used as a feed, the m/z=82 amu peak due to the corresponding reaction FCH<sub>2</sub>OH+2H→FCH<sub>3</sub>+H<sub>2</sub>O dominates, consistent



Figure 3.6. Comparison of experimental and simulated mass fragmentation spectra for furfuryl alcohol hydrogenolysis using fully deuterated 2-propanol as a hydrogen donor. Dominant contributions from fragments are shown. FCHDOD, formed by the MPV hydride transfer, is considered a reactant, where F is a furyl fragment  $C_4H_3O$ .

with this explanation. Agreement between simulated and experimental massspectroscopic peaks provides strong evidence for the radical C-O bond scission mechanism over RuO<sub>2</sub> vacancies.

# 3.8 Factors Governing the Reverse Mars van Krevelen Mechanism on RuO<sub>2</sub>(110) Vacancies

Due to the high reducibility of RuO<sub>2</sub> and weak Ru-O<sub>br</sub> bonds (Table B.2), the ability of RuO<sub>2</sub> vacancies to break the C-O bond and be oxidized by furfuryl alcohol is at first counterintuitive. Bond-breaking activity of a catalyst is usually attributed to the binding strength of the final products to the surface <sup>115</sup>; yet in the C-O hydrogenolysis, one of the products, furfuryl radical, interacts weakly with the surface. A higher OH binding energy on a RuO<sub>2</sub> vacancy than on Ru(0001) surface (-0.8 vs. -0.4 eV with respect to H<sub>2</sub>O and  $\frac{1}{2}$  H<sub>2</sub>) implies OH removal should be more difficult on RuO<sub>2</sub>. Contrast to our expectation, O/OH removal from metallic Ru is hard and vacancy formation on RuO<sub>2</sub> is very facile. We performed a detailed analysis of C-O bond hydrogenolysis energetics and identified three factors responsible for the unusual reactivity of RuO<sub>2</sub>.

First, the intact  $\pi$ -electron (aromatic) system in  $\beta$ -position to the C<sub>1</sub>-O bond in adsorbed furfuryl alcohol is essential for high hydrogenolysis rates. Fully saturated compounds, e.g., 2-propanol and tetrahydrofurfuryl alcohol, exhibit much higher C-O scission barriers (1.4 eV), and give limited activity in experiments<sup>148</sup>. To gain further insight into the role of aromaticity, in Figure 3.1 and Figure 3.7 we report the results of the Born-Haber energy decomposition analysis for C-O bond hydrogenolysis in the aromatic (furfuryl alcohol) and the corresponding aliphatic (tetrahydrofurfuryl alcohol) compounds. Starting with reactants in a vacuum and a hydroxylated RuO<sub>2</sub>(110) slab with a vacancy as an initial state, we separated the adsorption (E<sub>ads-reactant</sub>)/C-O scission (E<sub>IS-FS</sub>) reaction sequence into the following contributions (Figure 3.7b): (1) C-O scission in a vacuum with the frozen geometry of a furanic fragment (E<sub>C-O</sub>); (2) relaxation of the furanic radical in a vacuum (E<sub>relax</sub>); (3) adsorption of OH on a vacancy (E<sub>Ru-OH</sub>); and (4) adsorption of the furanic radical over OH (E<sub>ads-radical</sub>). Both furanic alcohols exhibit similar C-O bond scission energies in a vacuum (E<sub>C-O</sub> = 4.7-4.8 eV), due to cleavage of an ordinary bond. The two species primarily differ in the relaxation energies E<sub>relax</sub> of their radicals in a vacuum: -0.3 vs. -1.2 eV for saturated and unsaturated radicals, respectively. Relaxation of the radical entails sp<sup>3</sup>- to-sp<sup>2</sup> rehybridization of the C<sub>1</sub> atom; if the C<sub>2</sub> atom (β-carbon) is also sp<sup>2</sup>-hybridized, a favorable pp $\pi$  overlap occurs (conjugation) between the C<sub>1</sub>–localized p-orbital and the  $\pi$ -system of the furanic ring, as illustrated using Crystal Orbital Hamilton Population Analysis (COHP)<sup>149-151</sup> in Figure 3.8. Conjugation leads to delocalization of an unpaired electron (Figure 3.2) and stabilizes the furfuryl radical, effectively lowering the C-O scission barrier.

Reactant	Furfuryl alcohol	Tetrahydrofurfuryl alcohol
Eads-reactant	-0.8	-1.1
EIS-FS	0.1	1.4
Ec-o	4.8	4.7
E <sub>relax</sub>	-1.2	-0.3
E <sub>Ru-OH</sub>	-4.0	-4.0
Eads-radical	-0.3	-0.1

Table 3.1. Born-Haber decomposition of adsorption/C-O scission of furfuryl alcohol and tetrahydrofurfuryl alcohol over an oxygen vacancy. Energies in eV.

Unlike metals, where the furan ring strongly adsorbs on and partially loses its  $sp^2$  character, the ring does not form strong covalent bonds with the RuO<sub>2</sub> surface and retains its gas-like geometry (Figure B.4). Consequently, no side reactions (ring hydrogenation, decarbonylation, and ring opening) occur<sup>37</sup>; the furan aromatic ring remains intact under reaction conditions and facilitates C-O scission. Enhanced C-O scission rates have been related to the lack of  $\pi$ -system interaction with a metallic surface for furfuryl, benzyl<sup>152</sup>, and allyl alcohols<sup>153</sup> on a variety of catalytic systems, including Cu<sup>154-156</sup>, self-assembled monolayers on Pd<sup>157</sup>, H-covered Pd<sup>158</sup>, and partially oxidized Mo<sub>2</sub>C<sup>159,160</sup>. Taken this literature and our data together, the conjugation-assisted radical mechanism for activation of the C-O bond is a general one, provided that the  $\pi$ -electron system is preserved upon interaction of a molecule with a surface.



Figure 3.7. (a) C-O bond scission in furfuryl or tetrahydrofurfuryl alcohols; (b) Born-Haber cycle for C-O scission mechanism over an oxygen vacancy. R denotes either a furfuryl or a tetrahydrofurfuryl fragment.

The second crucial factor of the high RuO<sub>2</sub> activity is the anomalously high stability of the OH group on a vacancy. Ru(0001) surface and RuO<sub>2</sub>(110) vacancies differ in O binding energies (-0.5 vs. +0.8 eV; Table B.2). Universality of a linear scaling relationship between species binding energies for metals and oxides with octahedral coordination of ligands<sup>116,117</sup> implies that a RuO<sub>2</sub> vacancy should exhibit a OH binding energy of ~0.2 eV (0 eV for a hydroxylated surface). Contrary to the expectation, the OH binding energy is -1.1 eV (-0.8 eV on a hydroxylated RuO<sub>2</sub> surface). As a consequence, this strong binding significantly stabilizes the C-O scission intermediate (Figure 3.1).

The origin of the extraordinary stability of the surface hydroxyl is revealed by considering the OH formation from  $O_{br}$  and H as a two-step process<sup>161,162</sup>: (1)

excitation of an electron from an Olocalized valence band to a metallocalized conduction band, forming an O<sup>-</sup> surface radical; and (2)facile H abstraction by a radical. The energetics of step 1 has been shown to correlate with the electronic band gap for bismuth molybdates<sup>161,162</sup>; in addition, O-centered radicals were found to be crucial as abstracting sites for Η transfer reactions<sup>163</sup>. Due to the lack of the band gap in RuO<sub>2</sub>, surface O<sub>br</sub><sup>-</sup> radicals are stable already at the ground electronic state (Figure B.13), leading to high OH stability relative to Obr on RuO2



Figure 3.8. Crystal orbital Hamilton population (COHP) of the  $C_1$ - $C_2$  bond in furfuryl radical near the RuO<sub>2</sub>(110) surface. pp $\sigma$  overlap is denoted by green, pp $\pi$  overlap by red.

vacancies and consequently to high C-O scission rates.

Given that OH is so stable on RuO<sub>2</sub>, a natural question is why H+OH $\rightarrow$ H<sub>2</sub>O reduction on the metal involves a 1.3 eV energy barrier, whereas on RuO<sub>2</sub> the H<sub>2cus</sub> + O<sub>br</sub>H  $\rightarrow$  H<sub>cus</sub> + H<sub>2</sub>O<sub>br</sub> barrier is only 0.4 eV. First of all, water formation on the metal involves cleavage of strong M-H bonds (H binding energy of -3 eV on Ru(0001)), whereas on the oxide, H transfer to the neighboring hydroxyl occurs from adsorbed H<sub>2</sub> on Ru<sub>cus</sub>, in which antibonding orbitals are partially populated and the H-H bond is weakened<sup>164</sup> (the energy of removing H from H<sub>2,cus</sub> and leaving H<sub>cus</sub> on the surface is 2.6 eV). However, the major difference in water formation barriers stems from a

transition state (de)stabilization mechanism. On the metallic Ru, the high H+OH $\rightarrow$ H<sub>2</sub>O barrier is associated with overcoming Pauli repulsion during the O-H bond formation, which *destabilizes* the transition state<sup>165</sup>. On RuO<sub>2</sub>, two opposite ends of the H<sub>2</sub> molecule in the transition state interact with Lewis-acidic Ru<sub>cus</sub> and Lewis-basic O<sub>br</sub>H sites, forming a dipole (Bader charges -0.29 and +0.40, respectively). Consequently, favorable acid-base interaction reduces Pauli repulsion, and the transition state is stabilized by strong interaction with the surface (-2.1 eV with respect to H2 in a vacuum in its transition state geometry), which largely compensates the energy penalty arising from H-H bond stretching (0.9 eV) and slab deformation (1.1 eV). Therefore, the dual Lewis acid-base site nature of the RuO<sub>2</sub>(110) surface leads to facile reduction and removal of surface hydroxyls, constituting the third reactivity factor. In fact, vacancy formation via OH removal is too facile on RuO<sub>2</sub>, causing its rapid reduction under experimental conditions<sup>37,120</sup>. Therefore, optimization of oxide acid-base properties and hydroxyl stability will be essential for designing a more stable C-O hydrogenolysis catalyst.

### **3.9** Conclusions

We demonstrated that high 2-methyl furan yields achieved in catalytic transfer hydrogenation of furfural with 2-propanol stem from the interplay of three catalytic functionalities: RuO<sub>2</sub> Lewis acid sites that catalyze intermolecular hydride transfer, RuO<sub>2</sub> oxygen vacancies that promote C-O bond scission, and metallic Ru sites, which are essential for maintaining dissolved H<sub>2</sub> concentration and continuous vacancy regeneration. The most crucial step of the mechanism is ultrafast and selective reduction of the C-O bond over RuO<sub>2</sub> vacancies. We attribute the surprisingly high reduction activity of vacancies to a furfuryl radical intermediate. We employed an energy decomposition scheme and singled out three important factors governing catalyst activity toward C-O bond activation: favorable  $pp\pi$  orbital overlap in the furfuryl radical intermediate, which retains its  $\pi$ -electron system near the catalyst surface and is thus stabilized by conjugation; high hydroxyl affinity of RuO<sub>2</sub> vacancies, attributed to the RuO<sub>2</sub> metallic character and the presence of O<sup>-</sup><sub>br</sub> radical species in the ground state of the pristine surface; and acid-base heterogeneity of the surface, essential for H<sub>2</sub> dissociation and rapid vacancy formation. The radical mechanism is consistent with location-specific incorporation of deuterium into the furan ring in isotopic labeling experiments and explains reactivity trends among aromatic/aliphatic compounds. The mechanism extends to other catalytic and reaction systems, provided that unsaturated reaction intermediates weakly interact with catalytic surfaces and retain their conjugated  $\pi$ -electron orbitals. The discovered conjugation-driven mechanism opens up opportunities for an integrated design of reaction pathways and catalytic materials and can be beneficial for development of low-temperature catalytic processes, where small activation barriers are required.

### Chapter 4

# FUNDAMENTALS OF C-O BOND ACTIVATION ON METAL OXIDE CATALYSTS

### 4.1 Abstract

Fundamental knowledge of the active site requirements for selective activation of carbon-oxygen bonds over heterogeneous catalysts is required to design multistep processes for synthesis of complex chemicals. Here, we employ reaction kinetics measurements, extensive catalyst characterization, first principles calculations, and microkinetic modeling to reveal metal oxides as a general class of catalysts capable of selectively cleaving C-O bonds with unsaturation at the  $\alpha$ -position, at moderate temperature and H<sub>2</sub> pressure. Strikingly, metal oxides are considerably more active catalysts than commonly employed VIIIB and IB transition metal catalysts. We identify the normalized Gibbs free energy of oxide formation as both a reactivity and a catalyst stability descriptor and demonstrate the generality of the radical-mediated, reverse Mars-van Krevelen C-O bond activation mechanism on oxygen vacancies, previously established only for RuO<sub>2</sub>. We reveal that nearly all catalytic surfaces become hydrogenated in the reducing reaction environment and exhibit unexpected diversity in vacancy formation mechanisms. Importantly, we provide evidence that the substrate plays an equally key role to the catalyst in C-O bond activation.

# 4.2 Contributions

Konstantinos Goulas and Tobias Mazal designed and performed all experimental kinetic studies. Goulas designed and performed all characterization studies. Alexander Mironenko developed and analyzed microkinetic models and introduced a new thermodynamic referencing scheme. Mironenko performed the *ab initio* thermodynamics and DFT calculations. Glen Jenness assisted with DFT calculations. Dionisios Vlachos directed the project and provided guidance for the experimental and theoretical work. Goulas and Mironenko contributed equally.

# 4.3 Introduction

Selective carbon-oxygen bond activation in C<sub>2+</sub> molecules represents an essential part of the carbon-neutral, solar energy-based economy of the future. In biomass-mediated pathways, the initial CO<sub>2</sub> reduction and C-C coupling are carried out through the selective, albeit not very efficient (<3-4% solar-to-biomass energy conversion efficiency<sup>166</sup>), biochemical photosynthesis in photoautotrophic organisms. The resulting chemicals and bioproducts are typically over-oxygenated. Subsequently, selective C-O bond scission in fatty acids, glucose, glycerol, and furans is conducted to remove some of the excess oxygen. Typical catalysts used for deoxygenation are Ni or Co-modified MoS<sub>2</sub><sup>167-170</sup> or bifunctional Brønsted acid/noble metal catalysts.<sup>24,171</sup> Implementation of those catalysts for furanics has been problematic, as the former catalysts require undesired sulfides in the feed<sup>172</sup> and the latter catalyze overhydrogenation and decarbonylation (side reactions).<sup>173,174</sup> Recently, we discovered that RuO<sub>x</sub> is exceptional in activating the C-O bond and converting 2-hydroxymethylfurfural to 2,5-dimethylfuran<sup>175,176</sup> and furfural to 2-methylfuran (2MF)<sup>36,37</sup>. Lewis acidic sites on the RuO<sub>2</sub> carry out catalytic transfer hydrogenation

between an alcohol donor and the C=O of the furan,<sup>177</sup> and oxygen vacancies cleave the C-O bond of the side group via a reverse Mars-van Krevelen mechanism.<sup>178</sup> Firstprinciples calculations indicate that the aromatic group in the  $\alpha$ -position to C-O bond is essential to stabilize (via conjugation) a radical intermediate and lower the C-O scission barrier.<sup>178</sup> Importantly, the generality of the mechanism on other common metal oxides, despite their lower cost compared to noble metals, remains elusive. Accumulated experimental data over MoO<sub>x</sub><sup>100,179,180</sup> and Ru/TiO<sub>2</sub> for phenol derivatives<sup>181,182</sup> hint at metal oxides being a generic class of materials for *complete* deoxygenation to form hydrocarbons. Yet, the catalyst stability and active site requirements for *selective* activation of only certain C-O bonds remain the subject of debate in the literature.

Here, we combine extensive kinetic experiments, *ab initio* microkinetics, and *ex situ* and *operando* catalyst characterization studies to demonstrate that the vacancymediated reverse Mars-van Krevelen mechanism is generic for selective C-O bond cleavage in the  $\alpha$ -position to a  $\pi$ -electron system on oxides of both d-block and pblock metals. We show that the performance of a catalyst depends on its ability to form vacancies while remaining stable under reaction conditions. This tradeoff results in a volcano with the oxide Gibbs formation energy being a suitable reactivity and catalyst stability descriptor. We identify the reaction energy of surface OH disproportionation to form water and an oxygen vacancy on oxide surfaces with thermodynamically stable terminations in a H<sub>2</sub>-rich atmosphere (i.e., hydrogenated or non-hydrogenated) as an intrinsic catalyst reactivity descriptor, supporting surface vacancies as the active catalytic sites. We demonstrate the relations using furfuryl alcohol (FA) as model substrate and generalize the mechanism to other substrates, confirming that conjugation in the  $\alpha$  position to the C-O bond drives efficient and selective C-O cleavage, by stabilizing a radical-like transition state. Our results manifest the power of revealing the reaction mechanism on a substrate as a rational way toward heterogeneous catalyst and pathway discovery.

# 4.4 **Results and Discussion**

## 4.4.1 Correlation of Materials Properties to Reactivity and Stability

Sensitivity analysis of the Ru/RuO<sub>2</sub> *ab initio* microkinetic model (MKM; Section C.1) described previously,<sup>178</sup> indicates that lower thermodynamic stability of

surface hydroxyls relative to a vacancy, manifested on oxide materials with weaker M-O bonds, would lead to higher reaction rates of C-O cleavage. The fact that RuO<sub>2</sub> is reduced during reaction<sup>183</sup> also suggests that stronger M-O bonds would lead to more stable catalysts. In order to assess these hypotheses experimentally, we measure the reaction kinetics over RuO<sub>2</sub>, IrO<sub>2</sub>, PdO, and MoO<sub>3</sub> and determine their oxidation states before and after reaction using XRD and XPS or XAS. We focus first on FA as the model substrate (Scheme 1).



Scheme 1: Generic vacancymediated mechanism of the hydrodeoxygenation (HDO) of furfuryl alcohol (FA) to 2methyl furan (MF) over metal oxides.



Figure 4.1. Kinetics and characterization of selected oxide catalysts. (a)-(d) Reaction progress studies at 433 K, 0.1 M furfuryl alcohol in 96 mL toluene, 4.7 bar H<sub>2</sub> and 15 bar N<sub>2</sub>. (a) 0.1 g unsupported RuO<sub>2</sub>, (b) 1 g  $IrO_x/SiO_2$ , (c) 0.2 g PdO/SiO<sub>2</sub>, (d) 3 g unsupported MoO<sub>3</sub>. (e)-(h): Characterization of fresh and spent catalysts. (e) RuO<sub>2</sub> 3p XPS, (f) Ir L<sub>III</sub> edge XANES, (g) Pd 3d XPS, (h) Mo 3d XPS.

Consistent with our earlier results,<sup>176</sup> initial reaction rates over RuO<sub>2</sub> are high (Figure 4.1A). However, 2MF is converted at longer times (> 200 min), due to the reduction of RuO<sub>2</sub> to metallic Ru during reaction, as evident in the Ru 3p XPS results (Figure 4.1E), where the Ru  $3p_{3/2}$  peak shifts from 463.1 to 461.8 eV, causing facile ring opening over metallic Ru.<sup>184,185</sup> Similarly, IrO<sub>2</sub> gives high rates (Figure 4.1B) but undergoes partial reduction to metallic Ir. Linear combination fitting of the near-edge region of the XAS spectrum of the spent sample reveals that the catalyst is 56% reduced and 44% oxidized. The rate over a completely reduced Ir catalyst is lower by approximately five times<sup>186</sup>, indicating that the active catalyst is the oxide. PdO is rapidly converted to metal during heating, as the Pd 3d XPS (Figure 4.1G) suggests: the Pd  $3d_{3/2}$  peak shifts from 337.1 eV to 340.1 eV. Consequently, the observed rate (Figure 4.1C) is due to metallic Pd. As expected, the MoO<sub>3</sub> catalyst is stable (XPS data in Figure 4.1H and XRD data<sup>186</sup>), but significantly less active (Figure 4.1E) and leads to more byproducts.



Figure 4.2. Correlation of initial reaction rate of HDO with the free energy of oxide formation per oxygen atom. 433 K, 4.7 bar  $H_2$  and 15 bar  $N_2$ , 0.1 M furfuryl alcohol in toluene. Blue points are oxides, red points correspond to metals.

With an understanding from detailed characterization discussed above, we employ XRD before and after the reaction<sup>186</sup> to quickly classify several more catalysts into (1) stable materials (CeO<sub>2</sub>, TiO<sub>2</sub>, VO<sub>2</sub>, ZnO, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, MoO<sub>3</sub>), (2) partially reducible catalysts (RuO<sub>2</sub> and IrO<sub>2</sub>), and (3) rapidly reducible catalysts (CuO, Rh<sub>2</sub>O<sub>3</sub>, PdO, Ag<sub>2</sub>O, Au<sub>2</sub>O<sub>3</sub>).

Inspired by previous hydrodesulfurization (HDS) work<sup>187</sup>, Figure 4.2 shows the initial 2MF formation rate constant vs. the normalized (with the number of oxygen atoms in the formula unit) Gibbs free energy of the oxide formation  $(\Delta G_f)$ ,<sup>186</sup> with the latter used as a surrogate for the M-O bond strength. The rate displays a volcano-type behavior. On the left-hand side of the volcano ( $\Delta G_f < -1.4 \text{ eV}$ ), the activity of the catalyst increases with the weakening of the M-O bond. Similar correlations were observed when the rates were normalized by the number of oxygens per unit area of the most thermodynamically stable plane. The right-hand side of the volcano curve is populated with oxides whose M-O bonds are too weak and are reduced to metals at the start of the reaction. The reduction in the reaction rate with decreasing M-O bond strength is then attributed to the decreasing oxophilicity of the resulting metals that renders them less capable of cleaving C-O bonds.

*Operando* TPR/XANES measurements over MoO<sub>3</sub>, RuO<sub>2</sub>, IrO<sub>x</sub>/SiO<sub>2</sub>, and PdO<sub>x</sub>/SiO<sub>2</sub> (Figure 4.3) provide further evidence for the M-O-strength-dependent catalyst stability. MoO<sub>3</sub> remains completely oxidized after 40 min of reaction, PdO is completely reduced almost immediately, and RuO<sub>2</sub> exhibits a ~15 min induction period, followed by rapid reduction. A similar sigmoidal-shape reduction has been observed upon exposing a RuO<sub>2</sub>(110) thin film to  $10^{-4}$  to  $10^{-2}$  Pa of H<sub>2</sub> by spectroscopic ellipsometry.<sup>188</sup> Finally, the IrO<sub>x</sub>/SiO<sub>2</sub> is gradually reduced, reaching a plateau at approximately 60% extent of reduction, compared to 35% extent of reduction at reaction temperature<sup>186</sup>. Taken together (Figure 4.2 and Figure 4.3), our data indicate that the Gibbs free energy of formation is an appropriate descriptor of both the stability and the reactivity of oxide catalysts, superior to the more intuitive free energy change to the next stable phase<sup>186</sup>.

# 4.4.2 State of Catalyst Surfaces at the Reducing Environment

To gain atomistic understanding of the reducible oxide universality (Figure 4.2), we determined equilibrium surface terminations of model oxide surfaces under



Figure 4.3. Fraction of oxide as a function of temperature and time (TPR-XANES). Data of operando X-ray absorption spectroscopy from fitting the near-edge region of the spectrum (XANES). Blue points: Mo K edge; Green points: Ir  $L_{III}$  edge; Yellow points: Ru K edge; Red points: Pd K edge. 4.7 bar H<sub>2</sub>, 1 mL furfuryl alcohol in toluene, 10 °C/min from ambient to 473 K and hold. Dashed lines indicate qualitative trends. Vertical line corresponds to the batch reaction temperature.

the H<sub>2</sub>-rich experimental environment, i.e., whether surfaces are hydrogenated or pristine. Previous ultrahigh vacuum (UHV) studies revealed substantial hydrogen surface coverages on  $ZnO(10\overline{1}0)^{189}$ ,  $CeO_2(111)^{190}$ , and  $RuO_2(110)^{137}$  formed upon H<sub>2</sub> exposure already at ambient or sub-ambient temperatures, corroborating our assumption of fast and equilibrated H<sub>2</sub> dissociation, which can proceed through a "Lewis acid-base pair"-mediated, heterolytic splitting mechanism in the absence of metallic sites<sup>8,191</sup>. By minimizing the total Gibbs free energy of each surface with



Figure 4.4. Oxide surface terminations at the experimental  $H_2$  chemical potential. Blue bars indicate hydrogen coverage on exposed undercoordinated O atoms up to one monolayer (denoted as 1 ML H<sub>O</sub> at O<sub>br</sub>); red bars indicate additional hydrogen coverage on coordinatively unsaturated metal atoms up to one monolayer (1 ML H<sub>M</sub> at M<sub>cus</sub>). Examples of surfaces are shown on the right.

respect to the hydrogen coverage at the experimental H<sub>2</sub> chemical potential (see Sections C.2 and C.3), we reveal varying degrees of hydrogen coverage on oxide surfaces. While TiO<sub>2</sub>(100) stays pristine (Figure 4.4), TiO<sub>2</sub>(110) accommodates 0.33 monolayer (ML) H on bridging O sites (O<sub>br</sub>), consistent with its poor interaction with H<sub>2</sub> at UHV<sup>192</sup>, whereas ZnO(1010) exhibits full H coverage on both O and coordinatively unsaturated metal (M<sub>cus</sub>) sites, as observed experimentally at <200 K<sup>189</sup>. Similar to zinc oxide, IrO<sub>2</sub>(110), IrO<sub>2</sub>(101), and IrO<sub>2</sub>(100) are predicted to have both O<sub>br</sub> and M<sub>cus</sub> site types fully covered with hydrogen, whereas CeO<sub>2</sub>(111), RuO<sub>2</sub>(110), RuO<sub>2</sub>(101), RuO<sub>2</sub>(100), MoO<sub>3</sub>(100), and SnO<sub>2</sub>(110) expose fully capped O and unoccupied M<sub>cus</sub> sites. RuO<sub>2</sub>, IrO<sub>2</sub>, and TiO<sub>2</sub> demonstrate structural sensitivity of surface hydrogen affinities (Table C.10), which, however, does not lead to qualitative differences in the surface termination of the former two. Unexpectedly, the hydrogen affinity does not correlate with the band gap of the material (Table C.10), contrary to observations for bismuth molybdates<sup>162</sup>: interactions with hydrogen can be strong or weak for conductors with no band gap (RuO<sub>2</sub>, IrO<sub>2</sub>, VO<sub>2</sub>), or semiconductors (ZnO, TiO<sub>2</sub>). However, high hydrogen affinities of RuO<sub>2</sub> and IrO<sub>2</sub> conductors have implications on the vacancy formation mechanism and the surface reactivity descriptor, as shown below.

# 4.4.3 Surface Reactivity Descriptor

An optimal, easily computable surface reactivity descriptor should (1) account for stability differences of hydroxyl groups that are ubiquitous on oxide surfaces (Figure 4.4) and govern C-O bond scission reaction rates (Section C.1), and (2) involve species with an even number of electrons, due to the 2-electron transfer upon vacancy formation and the significance of the electron number parity to energetics of non-conducting materials<sup>193-195</sup> (Section C.4.3). This makes the commonly employed oxide descriptors (H-addition<sup>196</sup> and vacancy formation<sup>197</sup> energies; OH binding energies in analogy to SH binding for HDS<sup>198</sup>) inadequate for the vacancy-mediated C-O activation.

To unveil potential descriptor(s), we first developed an *ab initio*-based microkinetic model for TiO<sub>2</sub>(110) using an innovative energy referencing scheme to maintain the proper electron number parity (Section C.4.3). The model reproduces the experimental 2MF formation rate within an order of magnitude (3.6 vs. 1.1  $\mu$ mol/m<sup>2</sup>/h,

respectively) and predicts the FA reaction order in close agreement with the experimental value (0.94 vs. 0.70, respectively; Figure C.6). Reaction path analysis indicates that the vacancy formation proceeds via the quasi-equilibrated pool of surface intermediates, which can be reduced to disproportionation of two surface hydroxyl groups to form a vacancy and water ( $2OH_{br} \rightarrow O_{br}+V_{br}+H_2O$ ; Figure 4.5b; herein referred to as Type I reaction), which has been observed in the reverse direction on the reduced TiO<sub>2</sub>(110) interacting with water<sup>199</sup>. To generalize the TiO<sub>2</sub> MKM findings to other materials, we experimentally probed the dependence of the hydrodeoxygenation (HDO) rates over selected oxides on the FA concentration and observed a reaction order between 0.65 and 0.95 (Figure C.6). A simplified kinetic model (Section C.5) shows that reaction orders closer to 1 are indicative of the rate-limiting C-O scission and equilibrated vacancy formation on all oxides considered.

Motivated by this mechanistic similarity, we tested and confirmed the hypothesis that the energy  $\Delta E_{2OH}$  of Type I mechanism, computed on experimentally relevant surface terminations (Figure 4.4), is a reactivity descriptor. Figure 4.5a depicts a linear relationship between  $\Delta E_{2OH}$  and the experimentally measured (logarithmic) reaction rate. Evidently, the former is linearly related to the normalized Gibbs free energy of oxide formation (Figure 4.2). CeO<sub>2</sub> exhibits the largest  $\Delta E_{2OH}$ , consistent with its lowest activity; MOO<sub>3</sub> demonstrates facile vacancy formation via OH disproportionation and thus high activity. The absolute value of the slope for  $\ln r \propto \frac{\Delta E_{2OH}}{RT}$  is considerably less than 1 (0.08), evidently due to the correlation between the transition state energy of the intrinsic C-O scission step involving OH strongly bound to the vacancy<sup>8</sup> and  $\Delta E_{2OH}$ . Weaker OH binding both promotes vacancy formation and increases the C-O scission barrier, thus reducing the slope. The

existence of a surface reactivity descriptor associated to a vacancy supports the generality of the vacancy-mediated mechanism on these oxides.



Figure 4.5. (a) Logarithmic reaction rate plotted vs. the computed reaction energy of surface hydroxyl disproportionation relative to H<sub>2</sub>O and a vacancy, calculated on realistic oxide surface terminations. Rate units are  $\mu$ mol m<sup>-2</sup> h<sup>-1</sup>. (b) Vacancy formation mechanisms: Type I (OH disproportionation) occurs on oxides corresponding to blue data points: MoO<sub>3</sub>, SnO<sub>2</sub>, VO<sub>2</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>; and Type II occurs on oxides corresponding to red data points: IrO<sub>2</sub> and RuO<sub>2</sub>. Deviations of IrO<sub>2</sub> and RuO<sub>2</sub> data points are due to inapplicability of the OH disproportionation descriptor to oxides exhibiting the Type II vacancy formation mechanism.

Figure 4.5 indicates, unexpectedly, that two of the most active catalysts (RuO<sub>2</sub> and IrO<sub>2</sub>) do not follow the scaling relationship and exhibit simultaneously high  $\Delta E_{2OH}$  values (due to strong O-H bonds) and high HDO reaction rates. We attribute their unique behavior to a different vacancy formation mechanism that makes the  $\Delta E_{2OH}$  descriptor irrelevant for those materials. Previously, we discovered that the facile vacancy formation on RuO<sub>2</sub>(110) upon exposure to H<sub>2</sub> at UHV conditions at room temperature is associated with the concerted vacancy formation/heterolytic H<sub>2</sub> dissociation: H<sub>2,cus</sub>+OH<sub>br</sub>  $\rightarrow$ H<sub>cus</sub>+H<sub>2</sub>O<sub>br</sub> $\rightarrow$ H<sub>cus</sub>+V<sub>br</sub>+H<sub>2</sub>O (Figure 4.5b; herein referred as Type II mechanism)<sup>8</sup>. Reaction energy calculations (Table C.11) reveal that the Type II mechanism is feasible on all RuO<sub>2</sub> and IrO<sub>2</sub> facets considered, while being energetically inferior to Type I mechanism on other oxides. Since Type II mechanism involves 2 types of sites (M<sub>cus</sub> and O<sub>br</sub>) instead of one, the simple 1-site descriptor of  $\Delta E_{2OH}$  no longer governs the reactivity of RuO<sub>2</sub> and IrO<sub>2</sub>, consistent with the observed deviations in Figure 4.5.

### 4.4.4 Generality of Reaction Mechanism and Role of Substrate

The single bulk descriptor correlating the reaction rate over oxides, microkinetic modeling findings, as well as the similarity of the reaction orders,<sup>200</sup> provide strong support that the mechanism of C-O bond scission in FA is common over all oxides. In order to establish the generality for other substrates, we probed the C-O scission reaction of a number of aromatic alcohols (Figure 4.6). The data for these reactions follow similar trends to that of FA, supporting our hypothesis that the mechanism applies beyond unsaturated furances.



Figure 4.6. (a) HDO of benzhydrol, furfuryl alcohol, 4-methylbenzyl alcohol, cinnamyl alcohol and saturated derivatives. (b) Correlation of HDO rates of 4-methylbenzyl alcohol (black points), benzhydrol (red points), furfuryl alcohol (yellow points), and cinnamyl alcohol (green points) over various oxides indicated. 0.1 M alcohol in toluene, 160  $^{\circ}$ C, 12 bar H<sub>2</sub>.

To better understand the role of substrate, we correlated a property thereof with reactivity. We posited that the formation energy of the radical transition state in the C-O bond scission step should determine the rate as this is a late transition state (Section C.1). To this end, we correlated the homolytic C-O bond cleavage electronic energy in the gas phase (Table C.12) with the hydrodeoxygenation rates. As can be seen in Figure C.8, the rate drops as the formation of the radical species becomes less favorable.

In sharp contrast to the aromatic substrates, and consistent with the hypothesis of the conjugation-driven mechanism, the C-O scission reaction rates over MoO<sub>3</sub> for aliphatic cyclohexanemethanol and hydrocinnamyl alcohol are lower than the detection limit (0.01  $\mu$ mol m<sup>-2</sup> h<sup>-1</sup>). Consistently, the greater extent of surface reduction and the lack of bulk phase-change of MoO<sub>3</sub><sup>186</sup>, when hydrocinnamyl alcohol is the reactant, suggest that C-O bond scission is key to replenishing the surface O removed by H<sub>2</sub>.

### 4.4.5 Discussion

Our findings parallel those in hydrodesulfurization (HDS) chemistry, where the rate of HDS increases as the M-S bond decreases in strength from VS<sub>2</sub> to RuS<sub>2</sub> on the left of the volcano curve;<sup>201</sup> the reduction of noble metal oxides parallels that of Re and Ru sulfides.<sup>202,203</sup> Interestingly, monotonic correlations with the Gibbs free energies (or enthalpies) of formation, normalized by the number of O (or S) atoms<sup>187</sup>, are manifested for both processes consistent with a common vacancy-mediated reaction mechanism.

Furthermore, our results with various substrates clearly generalize for the first time earlier insights underscoring the necessity of resonance stabilization of the reaction intermediate for an energetically favorable reaction pathway.<sup>178</sup> Importantly, our results indicate that the molecular structure of the substrate is as important as the catalyst itself; a good catalyst for one substrate is poor for another. In turn, this indicates the importance of understanding the reaction mechanism prior to and use this, as is done herein, as a powerful means for searching for optimal catalysts.

Traditional, Sabatier-type volcanos arise as a compromise between bondbreaking and site-blocking catalyst propensities; surprisingly, our newly discovered volcano plot stems from a tradeoff between the catalyst's ability to form vacancies and activate C-O bonds and its stability under reaction conditions, which, to the best of our knowledge, has no prior analogs in heterogeneous catalysis. The ease of estimating the bulk material free energy paves the way to discovery of new stable and active catalytic materials. Surprisingly, we demonstrate that d-block and p-block metal oxides are significantly more active than commonly employed VIIIB and IB transition metal catalysts.

Volcanos involving surface-inherent descriptors stem from intrinsic correlations that limit catalyst activity, and breaking such relationships constitutes the Holy Grail of future catalyst design<sup>204</sup>. Herein, we demonstrate how a scaling relation can be naturally circumvented on a single catalytic site, which is known to be challenging<sup>205</sup>, via modification of a simple, 1-site vacancy formation mechanism in favor of a more complex, 2-site one on RuO<sub>2</sub> and IrO<sub>2</sub> (Figure 4.5). Although the reactivity of the latter is still governed by the bulk formation energy (Figure 4.2), utilization of more complex materials (e.g., mixed oxides) with locally modified surface sites should bypass this limitation and open avenues to even more active and stable C-O scission catalysts.

# 4.5 Methods

### 4.5.1 Experimental

### 4.5.1.1 Catalyst Preparation and Characterization

Apart from SnO<sub>2</sub> and RuO<sub>2</sub>, all unsupported catalysts were obtained commercially. SnO<sub>2</sub> was prepared according to the protocol of Li and Kawi;<sup>206</sup> briefly, Na<sub>2</sub>SnO<sub>3</sub> (Sigma) was dissolved in water and mixed with a solution of hexadecyl trimethylammonium bromide (Sigma). The pH was adjusted to 8 using HCl and NH<sub>4</sub>OH, and the slurry was stirred at 368 K for 72 h. The solids were separated by centrifugation and subsequently treated in stagnant ambient air for 4 h at 823 K (at a ramp rate of 1 K min<sup>-1</sup> from ambient). Anhydrous RuO<sub>2</sub> was prepared by treating ruthenium oxide hydrate (Alfa Aesar) under flowing nitrogen (100 ml min<sup>-1</sup> g<sup>-1</sup>) at 573 K for 3 h (ramp rate 5 K min<sup>-1</sup>).

Supported oxides, 1.8% IrO<sub>2</sub>/SiO<sub>2</sub>, 1.5% RuO<sub>2</sub>/SiO<sub>2</sub>, 4.5% PdO/SiO<sub>2</sub>, and 1.6% RhO<sub>x</sub>/SiO<sub>2</sub>, were prepared by incipient wetness impregnation of an aqueous solution of the appropriate precursors onto silica gel (Davisil grade 60, Sigma Aldrich). The precursors used were H<sub>2</sub>IrCl<sub>6</sub> (Alfa Aesar), Ru(NO)(NO<sub>3</sub>)<sub>3</sub> (1.5% solution in dilute nitric acid, Alfa Aesar), Pd(NO<sub>3</sub>)<sub>2</sub> (8% aqueous solution, Alfa Aesar), RhCl<sub>3</sub> · xH<sub>2</sub>O (Sigma Aldrich), respectively. Following impregnation, the solids were held at ambient temperature and pressure for 24 h and were subsequently treated in stagnant ambient air at 673 K for 3 h (at a ramp rate of 5 K min<sup>-1</sup> from ambient). Another batch of catalysts was treated in a 50% H<sub>2</sub>/N<sub>2</sub> mixture (100 ml min<sup>-1</sup> g<sup>-1</sup>) at 573 K for 3 h (a ramp rate of 5 K min<sup>-1</sup> from ambient). This calcination or reduction enables us to compare the activities of the oxides and their corresponding

reduced metal catalysts. After reaction, the spent catalysts were recovered by filtration, washed with acetone, and finally dried at ambient temperature and pressure.

The metal oxide content of the supported catalysts was determined by X-ray fluorescence spectroscopy (XRF), using a Rigaku Miniflex instrument. The surface area of the unsupported catalysts was measured using nitrogen physisorption in an ASAP 2020 automatic physisorption instrument (Micromeritics, Norcross, GA). Prior to measurement, the samples were degassed under vacuum for 4 h at 523 K. The surface area was quantified by fitting the BET equation over seven  $p/p_0$  points using the instrument software.

The phase composition of the catalysts was determined using X-ray diffraction (XRD). A Bruker D8 Advance diffractometer was utilized, scanning from  $2\theta = 20$  to 70°. This same instrument was used for the estimation of the surface area of the supported oxides (except for RhO<sub>x</sub>/SiO<sub>2</sub>, whose particles were too small to be detected by XRD). This was achieved by measuring the full width at half maximum of the peaks and applying the Scherrer equation. The surface area of the supported catalysts was then estimated by assuming hemispherical particles on the support.

The surface area of  $Rh_2O_3$  on the SiO<sub>2</sub> support was determined by transmission electron microscopy (TEM). The catalyst was ground and dispersed in acetone and the dispersion was sonicated for 1 min. Then, 10 µL of the solution were drop-cast onto a Cu TEM grid. Imaging was carried out in a JEOL JEM3010 electron microscope at 300 kV.

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Thermo Scientific Kalpha+ instrument. The instrument was equipped with an Al K<sub>a</sub>

anode, and the pressure of the analysis chamber was kept lower than  $10^{-5}$  Pa. Prior to analysis, powdered samples were spread on a conductive carbon tape.

X-ray absorption spectroscopy (XAS) experiments were performed at the Advanced Photon Source (APS) at Argonne National Lab (ANL), beamline 5BM-D; and at the Stanford Synchrotron Radiation Lightsource (SSRL), beamline 2-2. The data were processed with the Demeter suite; to obtain oxidation states of the catalysts, the near-edge region of the spectrum (XANES) was fitted with appropriate standards (metal foils and oxides).

Ir L<sub>III</sub> edge XAS measurements were carried out in transmission for the fresh, spent, and reduced  $IrO_x/SiO_2$  catalysts at the APS. For these measurements, the samples were pressed into self-supporting wafers in a multiple-well sample holder. Sample loadings were calculated for total absorption  $\Delta \mu = 2$ , to avoid self-absorption effects. Samples were scanned at ambient conditions and the spectra recorded using sealed ionization chambers (Danfysik).

*Operando* temperature-programmed reaction (TPR) combined with X-ray absorption was performed at the APS in transmission, using a stainless steel cell with glassy carbon windows. In these experiments, the catalyst was loaded into a PEEK basket and placed in the cell. Then, the cell was filled with the reactant solution, purged with  $N_2$  and pressurized with  $H_2$  to a pressure of 4.7 bar. Then, the temperature was increased from ambient to 473 K at a rate of 10 K/min, while spectra were recorded. The temperature was held at 473 K for at least 30 min.

Finally, the oxidation state of  $IrO_x/SiO_2$  was measured under reaction conditions in a Clausen cell using XAS at the SSRL. 5 mg of catalyst were packed in a 3 mm OD polyimide ("Kapton") tube and secured in position with glass wool. The

outlet of the cell was sealed and the tube filled with the reactant solution. The cell was then purged with He and then pressurized with  $H_2$  to 4.7 bar. Then the cell was heated to 433 K in 1 min and held for 3 h while spectra were recorded using flowing gas ionization chambers.

### 4.5.1.2 Reaction Rate Estimation and Species Quantification

HDO reaction rates were measured in a stainless steel stirred batch reactor (Parr Instrument Co., Moline, IL). The catalyst was loaded in the reactor, together with 96 mL of toluene, and the reactor was pressurized with 4.7 bar hydrogen. The system was subsequently heated to 433 K under stirring, and 4 mL of toluene solution, containing 0.98 g FA, was injected using nitrogen pressure (15 bar). Samples were taken using a 1.6 mm stainless steel tube, which was cooled to ambient temperature using a water bath. Before each sample, the tube was purged with 3 mL of solution. The initial rate  $(r_{HDO})$  was quantified by fitting a straight line to the 2MF concentration/time plot at low conversions and dividing by the catalyst surface area. For this calculation, only data points that corresponded to conversions lower than 15% were used. The reaction rate constant ( $k_{HDO}$ ) was calculated by dividing the initial rate by the concentration of furfuryl alcohol. Speciation and quantification of chemical species in the solution was achieved using gas chromatography. For quantification, we used an Agilent 7890B GC, equipped with an Innowax column (30 m x 0.25 µm x 0.25 mm) and a flame ionization detector. Retention times and response factors were calibrated using standard solutions of known concentrations. Unknown compounds were identified using a Shimadzu GC2010 GC/MS, with an Innowax column identical to the one in the GC.
# 4.5.2 Computational

All calculations utilized density functional theory (DFT) as implemented in the Vienna ab-initio simulation package (VASP, version 5.3.5).45,207-209 The Perdew-Burke-Ernzerhof exchange-correlation energy functional (PBE)<sup>210</sup> was employed for the valence electrons, whilst the core electrons were represented using the projector augmented wavefunction (PAW) method.<sup>211</sup> The DFT+U scheme by Dudarev et al.<sup>212</sup> was applied to correct for the electron delocalization error in localized d-states of (U values are given in parentheses):  $TiO_2$  (3.5 eV, taken as a value between 3.3 and 3.9 eV<sup>213</sup>), SnO<sub>2</sub> (3.5 eV<sup>214</sup>), ZnO (4.7 eV<sup>215</sup>), MoO<sub>3</sub> (2.0 eV<sup>216</sup>), and f-states of CeO<sub>2</sub> (5.0  $eV^{217,218}$ ). No U parameter was used in TiO<sub>2</sub>(110) calculations for the microkinetic model parameterization (Section C.4). We used conventional valence configurations for Ir, Zn, O, H, and Ce. The semi-core s- and p-states were included as valence for Ti, V, and Mo; p semi-core states were included for Ru, and d semi-core states for Sn. All calculations were spin-polarized. Lattice constants for each oxide were optimized with a conjugate gradient algorithm until the Hellman-Feynman forces became lower than 0.01 eV Å<sup>-1</sup>. In all lattice optimizations, valence states were expanded in a plane wave basis set using an energy cutoff of 600 eV, and a self-consistency criterion of 10<sup>-8</sup> eV was employed. The Brillouin zone was sampled using a Monkhorst-Pack grid <sup>219</sup> with 3x3x3 k-points along corresponding reciprocal vector directions. The structure of TiO<sub>2</sub>, RuO<sub>2</sub>, IrO<sub>2</sub>, VO<sub>2</sub>, and SnO<sub>2</sub> was the tetragonal (rutile) structure, of ZnO the hexagonal wurtzite, of  $CeO_2$  the cubic fluorite, and of  $MoO_3$  the orthorhombic. We model VO<sub>2</sub> in its rutile structure, since the reaction temperature (433 K) is greater than the monoclinic  $\rightarrow$  rutile phase transition temperature (~339 K).

Periodic slabs for the most thermodynamically stable facets were employed as catalyst models. Slabs consisted of 4 stoichiometric layers for  $TiO_2(110)$ ,  $RuO_2(110)$ ,

IrO<sub>2</sub>(110), VO<sub>2</sub>(110), SnO<sub>2</sub>(110), CeO<sub>2</sub>(111) and ZnO(10 $\overline{1}$ 0). MoO<sub>3</sub>(100) was modeled as a ribbon formed after a 2-layer MoO<sub>3</sub>(010) slab was cut in half perpendicular to the (100) direction. The choice for MoO<sub>3</sub>(100) instead of the more thermodynamically stable MoO<sub>3</sub>(010)<sup>216</sup> was motivated by the availability of exposed, coordinatively unsaturated metal atoms on the former that are needed for efficient heterolytic hydrogen dissociation<sup>178,220</sup>. Preliminary calculations (not shown) indicate that the MoO<sub>3</sub>(010) O-terminated basal plane is unable to dissociate H<sub>2</sub>, which is consistent with the high-temperature onset of MoO<sub>3</sub> reduction (400 °C),<sup>221</sup> unless metal nanoparticles are present (e.g., Ir<sup>222</sup>) to promote H<sub>2</sub> dissociation.

In calculations, the bottom stoichiometric layer was frozen, and all the remaining atoms were relaxed, except for MoO<sub>3</sub>, for which all atoms were relaxed. The lateral oxide dimensions were p(3x2) for TiO<sub>2</sub>, RuO<sub>2</sub>, IrO<sub>2</sub>, VO<sub>2</sub>, SnO<sub>2</sub>; p(3x3) for MoO<sub>3</sub>, p(3x2) for ZnO, and (4x4) for CeO<sub>2</sub>. A vacuum layer of 20 Å separating periodic slab replicas in the *z*-direction was employed in all calculations. We used the  $10^{-4}$  eV self-consistency criterion, 400 eV kinetic energy cutoff and (3x2x1) k-point mesh for IrO<sub>2</sub>, RuO<sub>2</sub>, SnO<sub>2</sub>, VO<sub>2</sub>; (2x2x1) mesh for TiO<sub>2</sub>, and  $\Gamma$ -point Brillouin zone sampling for MoO<sub>3</sub> and CeO<sub>2</sub>. Optimal k-point meshes were determined by independent screening along  $k_x$  and  $k_y$  directions until change in the total slab energy was less than 0.05 eV. Geometry-optimization force-criterion was set to 0.05 eV/Å. All calculated structures are available in the Supporting information.

The relative thermodynamic stability of fully hydrogenated vs. clean surfaces was calculated using the procedure outlined in Section C.3. The  $H_2$  chemical potential was computed using the ASPEN Plus software at experimental reaction conditions – the detailed procedure is described in Section C.2. No species other than  $H_2$  are

considered in equilibrium calculations, as direct reactions between H-terminated  $RuO_2(110)$  surface and oxygenates have been ruled out.<sup>178</sup>

We excluded ZnO( $10\overline{1}0$ ) from vacancy formation energy calculations (Figure 4.5), as the nondirectional s-s interaction of H and Zn atoms facilitates H diffusion into the bulk above 200 K<sup>189</sup>, making a realistic description of the experimentally relevant ZnO structure difficult.

Details of the  $TiO_2(110)$  microkinetic model and the new referencing procedure are provided in Section C.4.

# 4.6 Conclusions

With insights about the reaction mechanism as a guiding catalyst design principle, we established experimentally and theoretically for the first time metal oxides as a generic class of catalysts for activating C-O bonds of unsaturated furanic derivatives of lignocellulosic biomass. Through kinetic and extensive characterization studies, we demonstrated that the Gibbs free energy of oxide formation is an appropriate descriptor for catalyst stability and activity in C-O bond scission, with remarkable similarity to that reported in hydrodesulfurization chemistry. This volcano correlation arises from a tradeoff between the ease of vacancy formation, leading to higher C-O scission rates, and oxide reduction, resulting in metal-like activity. Using first-principles calculations, the states of catalyst surfaces in the reducing reaction environment are revealed, and the remarkable diversity of vacancy formation mechanisms is exposed. Finally, we demonstrate for the first time the importance of the substrate and specifically that unsaturation in the  $\alpha$  position to the C-O bond, resulting in stabilization of the radical C-O bond scission transition state, is a general molecular trait – beyond furanics – for vacancy-catalyzed C-O cleavage. Promoting conjugation in reaction intermediates of multistep transformations, while modulating redox properties of an oxide, uniquely enables simultaneous design of optimal reaction pathways and catalysts. Our work introduces a successful example of how mechanistic insights and reactivity concepts (conjugation, vacancies as catalytic sites), established for just one material (RuO<sub>2</sub>), can be successfully extrapolated to a variety of materials and substrates, leading to discovery of a new class of catalysts. We expect these results to guide further developments in catalyst design.

### Chapter 5

# MECHANISMS FOR HIGH SELECTIVITY IN HYDRODEOXYGENATION OF 5-HYDROXYMETHYLFURFURAL OVER PTCO NANOCRYSTALS

#### 5.1 Abstract

Carbon-supported, Pt and PtCo nanocrystals (NCs) with controlled size and composition were synthesized and examined for hydrodeoxygenation (HDO) of 5hydroxymethylfurfural (HMF) by Gorte and Murray labs at the University of Pennsylvania. Experiments in a continuous flow reactor with 1-propanol solvent, at 120 to 160°C and 33 bar H<sub>2</sub>, demonstrated that reaction is sequential on both Pt and PtCo alloys, with 2,5-dimethylfuran (DMF) formed as an intermediate product. However, the reaction of DMF is greatly suppressed on the alloys, such that a  $Pt_3Co_2$ catalyst achieved DMF yields as high as 98%. Our data-driven, mean field structural catalyst model identified the Pt<sub>3</sub>Co<sub>2</sub> catalyst with a Pt-rich core and a unique Co oxide surface monolayer to be consistent with all experimental characterization data, such as TEM, XRD, and XAS. We find that the oxide monolayer structure differs substantially from that of bulk Co oxide. Density functional theory (DFT) calculations reveal that the oxide monolayer interacts weakly with the furan ring to prevent side reactions, including over-hydrogenation and ring opening, while providing sites for effective HDO to the desired product, DMF. We demonstrate that control over metal nanoparticle size and composition, along with operating conditions, is crucial to achieving superior performance and stability. Implications of this mechanism for other reactions and catalysts are discussed.

# 5.2 Contributions

Jing Luo and Cong Wang carried out HDO kinetic studies. Hongseok Yun and Jennifer Lee performed catalyst synthesis and characterization. Konstantinos Goulas carried out XAS characterization. Alexander V. Mironenko developed a structural model of a catalyst consistent with all experimental characterization data and performed mechanistic DFT investigations pertinent to the Pt<sub>3</sub>Co<sub>2</sub> catalyst. Vassili Vorotnikov investigated an HDO reaction network for the Pt catalyst. Christopher B. Murray, Paolo Fornasiero, and Raymond J. Gorte directed the experimental portion of work. Dionisios G. Vlachos directed the computational aspect of the work. Luo, Yun, and Mironenko contributed equally. For a complete version of the paper, we refer a reader to ref.<sup>9</sup>

# 5.3 Introduction

5-Hydroxymethylfurfural (HMF) is a key platform chemical in biomass conversion.<sup>223,224</sup> It is readily obtained by the acid-catalyzed dehydration of C-6 sugars (e.g, fructose, but its high degree of functionality precludes its direct use as a fuel.<sup>225-227</sup> One promising approach to stabilize HMF is the selective hydrodeoxygenation to form 2,5-dimethylfuran (DMF). A relatively small amount of hydrogen is consumed in the formation of DMF and DMF can be used directly as fuel additive due to its high energy density and an octane rating of 119.<sup>228</sup> DMF can also be converted to p-xylene via a Diels-Alder reaction with ethylene.<sup>229</sup>

The reaction of HMF to DMF has been studied extensively over various metal and metal-alloy catalysts<sup>175,230,231</sup>, but selectivity to DMF over ring-opened (e.g. 2hexanone, 2,5-hexanedione) and ring-hydrogenated (e.g. 2,5-dimethyl tetrahydrofuran) products is often poor. More recent reports indicate that bimetallic catalysts tend to be more selective than their pure-metal analogs.<sup>95,232,233</sup> For example, Schüth and co-workers<sup>234</sup> reported DMF yields as high as 98% on Pt-Co nanoparticles which were encapsulated in hollow carbon spheres. However, atomistic understanding of optimal catalytic site structure that enables high DMF yields is currently lacking.

Herein, we report the HDO of HMF into DMF catalyzed by Pt, Pt<sub>3</sub>Co, and Pt<sub>3</sub>Co<sub>2</sub> NCs. DMF yields as high as 98% are achieved in HDO of DMF using a continuous flow reactor with Pt<sub>3</sub>Co<sub>2</sub> alloys, because this alloy shows a very low reactivity towards DMF. A combination of structural modeling, state-of-the-art characterization methods, and high-precision solvothermal NC synthesis revealed Pt-Co NCs to have a special structure consisting of a monolayer of surface oxide on a metallic core. Calculations using Density functional theory (DFT) rationalize the stability of this structure and indicate that the oxide prevents side reactions while providing catalytic sites for effective conversion of HMF to DMF. Computations reveal a radical-mediated reaction mechanism, which some of us have found to be critical for selective HDO on oxides.<sup>8</sup> Structural characterization and DFT calculations confirm that controlling the bimetallic composition is essential for preparing a good catalyst.

### 5.4 Density Functional Theory (DFT) Methodology

Spin-polarized density functional theory calculations have been carried out under the generalized gradient approximation using VASP software<sup>43,45,46</sup>. Kohn-Sham eigenstates have been expanded in a plane wave basis set with a kinetic energy cutoff of 400 eV. Sampling of the first Brillouin zone has been carried out according to the Monkhurst-Pack<sup>51</sup> 3x3x1 k-point mesh. The initial magnetic moment of Co atoms has been set to 2.0 Bohr-magnetons. Exchange, correlation, and dispersion effects have been approximated with a PBE-D3<sup>14,235</sup> functional. Threshold value for maximum atomic forces has been set to 0.05 eV/Å. Transition states have been identified via a climbing-image nudged elastic band (CINEB) and/or a dimer<sup>18-21</sup> method with the forces' tolerance set to 0.1 eV/Å. A honeycomb  $Co_3O_2$  on a Pt-rich metallic core has been modeled as a  $Co_3O_2/Pt(111)$  surface using a (4x4) supercell with a honeycomb  $Co_3O_2$  structure placed on top of three Pt layers (bottom two were fixed).We used a finite difference method to calculate selected vibrational frequencies. Throughout the paper, DFT energies in a vacuum are reported, unless stated otherwise.

# 5.5 Results

# 5.5.1 Experimental Data Summary

### 5.5.1.1 Catalyst Synthesis and Initial Characterization

Nearly monodisperse Pt, Pt<sub>3</sub>Co, and Pt<sub>3</sub>Co<sub>2</sub> NCs were synthesized by using or modifying the reported colloidal synthesis methods,<sup>236,237</sup> using platinum (II) acetylacetonate (acac) and dicobalt octacarbonyl (Co<sub>2</sub>(CO)<sub>8</sub>) as catalyst precursors; benzyl ether as a solvent; and oleic acid, oleylamine, trioctylphosphine, 1-adamantane carboxylic acid, 1,2-hexadecanediol (HDD), and hexadecylamine as protective ligands, additives, and/or reductants. From the Transmission Electron Microscope (TEM) data, the average diameters of NCs were 2.4 nm, 3.2 nm, and 3.7 nm with less than 8% of size distribution for Pt, Pt<sub>3</sub>Co, and Pt<sub>3</sub>Co<sub>2</sub> NCs, respectively. An observed superlattice structure indicated the high monodispersity of these NCs. Wide angle x-ray scattering data show that all the NCs possess face-centered cubic (fcc) crystal structure. The compositions of NCs were confirmed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

The NCs are dispersed into carbon support to prepare 10 weight % of metals on carbon. To remove the ligands and expose catalytic sites, the catalysts were exposed to  $O_2$  plasma for 15 mins, followed by rapid thermal annealing (RTA)<sup>238</sup> with no change in phase, size, and morphology.

The metal dispersions were determined volumetrically using CO adsorption uptakes at room temperature on  $Al_2O_3$  supported catalysts, assuming an adsorption stoichiometry of one CO molecule per surface Pt.<sup>239</sup> Chemisorption of CO on Co was not included in the calculation of the dispersion, because control experiments on Co/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by impregnation method reduced at 400°C, did not show any CO adsorption.

# 5.5.1.2 Liquid-phase HDO with H<sub>2</sub> in a Flow Reactor

The three-phase reactions were carried out in a continuous flow reactor that has been described in detail elsewhere.<sup>173,240</sup> The liquid feed composition was either 1.0 g HMF or 0.76 g DMF in 100 mL of 1-propanol Prior to rate measurements, the catalyst was pretreated at 250°C in 1 bar of flowing H<sub>2</sub> for 30 min. The carbon balance from GC analysis was always better than 95%. The typical time for an experiment was 4 h.

Previous studies on carbon-supported Pt and Co catalysts have shown that hydrodeoxygenation of HMF to DMF is a series reaction<sup>173</sup>, proceeding as indicated in Scheme 1. The HMF (A) first reacts to a group of partially hydrogenated intermediate compounds (B), including 2-propoxymethyl-5-furanmethanol (ether-furfuryl alcohol, or EFA), 2-propoxymethyl-5-methylfuran (ether-methyl furan, or EMF), 5-methyl furfural (MF), 2-hydroxylmethyl-5-methyl furan (HMMF), 2,5bis(hydroxymethyl)furan (BHMF), and 2,5-bis(propoxymethyl)furan (BEF). These intermediate compounds can all be converted to DMF (C), which in turn reacts to over-hydrogenated products (D), dimethyl tetrahydrofuran (DMTHF), 2-hexanone, 2-hexanol, 2,5-hexanedione, and their etherification derivatives, 1-propoxy-1-methyl-pentane (2-propoxyhexane) and 1,4-dipropoxy-1,4-dimethyl-butane (2,5-dipropoxyhexane).



Scheme 1. Reaction network for HMF hydrodeoxygenation using alcohols as solvent.

The mechanism is also confirmed for 10 wt. % Pt/C prepared from Pt NCs, which are found to be considerably more active than Pt catalysts obtained through impregnation. Figure 5.1a depicts the conversion and product yield as a function of space time at 120°C, significantly lower than used in the previous study. <sup>173</sup> Even for the shortest space time and at this low temperature, the HMF conversion was greater than 65%. Initially, partially hydrogenated products, B, were formed in the highest yields, but these declined steadily with increasing space time. DMF yield initially increased, then decreased, providing strong evidence that DMF is an intermediate product in a series reaction. The maximum yield was approximately 41%. Overhydrogenated compounds, D, only formed at higher space times, indicating that they

are not primary products. The fact that their formation follows the consumption of DMF strongly suggests they are formed from DMF.



Figure 5.1. Conversion and product distribution for the HDO reaction of HMF over (a) 10-wt% Pt/C, (b) 10-wt% Pt<sub>3</sub>Co/C, (c) 10-wt% Pt<sub>3</sub>Co<sub>2</sub>/C, as a function of reactor space time. Reaction conditions: 33 bar and 120 °C. ( $\mathbf{\nabla}$ ) HMF conversion, ( $\mathbf{\Delta}$ ) product group B, ( $\mathbf{\Theta}$ ) DMF, ( $\mathbf{\Box}$ ) product group D.

Similar experiments were performed on the 10 wt-% Pt-Co, NCs catalysts, with Pt:Co ratios of 3:1 and 3:2. Data at 120°C and 33 bar are shown in Figure 5.1b and 5.1c. For a given space time, the HMF conversions over the Pt<sub>3</sub>Co in Figure 2b were slightly lower than that obtained on the pure Pt NCs; but the initial products were the same partially hydrogenated compounds, B, with these again being converted to DMF at a similar rate. However, on the Pt<sub>3</sub>Co catalyst, the DMF yield continued to

increase, to a value of 75%; and only relatively small quantities of over-hydrogenated compounds, D, were formed at the largest space times. The activity of the  $Pt_3Co_2$  catalyst was noticeably lower than that of the other two samples, and 100% conversion of HMF was achieved only at the highest space time. Because of the lower activity, the DMF yield was still increasing at the highest space time, and the production of D-group compounds was negligible.

Due to the lower rates on the Pt-Co catalysts, additional reaction measurements were performed at 160°C and 33 bar in order determine the evolution of products, with results shown in Figure 5.2. As shown in Figure 5.2a, the HMF conversion was nearly 90% on the Pt<sub>3</sub>Co sample, even at the lowest space time. The B-products again decline steadily with time but DMF yield went through a maximum of about 75% at this temperature, with over-hydrogenated products being produced from the DMF. However, results for the Pt<sub>3</sub>Co<sub>2</sub> sample in Figure 5.2b show the DMF yields continuing to increase, up to 98%.



Figure 5.2. Conversion and product distribution for the HDO reaction of HMF over (a) 10-wt% Pt<sub>3</sub>Co/C, (b) 10-wt% Pt<sub>3</sub>Co<sub>2</sub>/C, as a function of reactor space time. Reaction conditions: 33 bar and 160 °C. ( $\mathbf{\nabla}$ ) HMF conversion, ( $\mathbf{\Delta}$ ) product group B, ( $\mathbf{\Theta}$ ) DMF, ( $\mathbf{\Box}$ ) product group D.

The  $Pt_3Co_2$  sample was also very stable compared to the Pt catalyst. Figure 5.3 shows the HMF conversion and DMF yield for the two catalysts as a function of time at 160°C and a space of 1.0 g·min/mL. The Pt-Co catalysts has no observable

deactivation or change in selectivity for a period of at least 14 h. By contrast, the Pt/C deactivated rapidly under these same conditions. It should be noted that Pt/C catalyst was highly active under these conditions, so that the low initial yield is due to the "over-reaction" of DMF over-hydrogenated to (D) compounds. The increasing yield with short times results from the lower catalyst activity. In addition to the stability against coking, the alloy catalyst is also more thermally stable.<sup>241</sup> TEM images (not shown) indicate that



Figure 5.3. Time on stream measurements for HMF hydrodeoxygenation. Reaction conditions: 33 bar, 160 °C, W/F 1.0  $g \cdot min/mL$ . (**II**) HMF conversion over 10wt% Pt<sub>3</sub>Co<sub>2</sub>/C, ( $\triangle$ ) DMF yield over 10-wt% Pt<sub>3</sub>Co<sub>2</sub>/C, (**IV**) HMF conversion over 10wt% Pt/C, ( $\nabla$ ) DMF yield over 10-wt% Pt/C.

after 5 hours reaction at 160°C the average size of Pt NCs increased and some aggregates formed, while the size and shape of Pt<sub>3</sub>Co<sub>2</sub> NCs remained unchanged.

The results in Figure 5.1 and Figure 5.2 indicate that Co alloying with Pt has a modest effect on HDO rates for HMF but strongly suppresses reactions of DMF. To investigate this in more detail, we examined the reaction of DMF on the same three catalysts, with conversions and product distributions shown in Figure 5.4. DMF is converted rapidly on Pt/C, even at 120°C. The main products are the open-ring

ketones and ethers, the products that were also formed at high space times for the reaction of HMF.<sup>9</sup> DMF conversions on the  $Pt_3Co$  sample were lower than that observed on the Pt catalyst even at higher reaction temperature (160°C), although still significant. The products on the  $Pt_3Co$  catalyst were essentially the same as that observed on Pt. However, the conversion of DMF on the  $Pt_3Co_2$  sample at 160°C, shown in Figure 5.4c, was very low for all space times, reaching a value of only 10% at a space time of 1.0 g·min/mL.



Figure 5.4. Conversion and product distribution for the reaction of DMF as a function of space time at 33 bar: (a) 10-wt% Pt/C at 120 °C; (b) 10-wt% Pt<sub>3</sub>Co/C at 160 °C, (c) 10-wt% Pt<sub>3</sub>Co<sub>2</sub>/C at 160 °C. ( $\nabla$ ) DMF conversion, ( $\Box$ ) DMTHF, ( $\nabla$ ) 2-hexanone, 2-hexanol and 2-propoxyhexane, ( $\triangle$ ) 2,5-hexandione, 2,5-dipropoxyhexane, ( $\bigcirc$ ) hexane.

#### 5.5.1.3 Catalyst Characterization

In order to understand the role of Co for high HMF-to-DMF selectivity and elucidate the nature of the active site, a combination of microscopic, spectroscopic, and computational tools were employed, as discussed below. Wide angle x-ray scattering data (not shown) show that the (220) peak shifts from 67.6° for Pt NCs to  $68.2^{\circ}$  and  $68.4^{\circ}$  for Pt<sub>3</sub>Co and Pt<sub>3</sub>Co<sub>2</sub>, indicating the replacement of Pt by Co in the lattice structure. The lattice constants of the NCs, determined from the position of the (220) peak on the x-ray scattering patterns, are 3.92, 3.87, and 3.87 Å for Pt, Pt<sub>3</sub>Co, and Pt<sub>3</sub>Co<sub>2</sub> NCs, respectively. Using Vegard's law, the bulk Co fraction in the Pt<sub>3</sub>Co and Pt<sub>3</sub>Co<sub>2</sub> NCs is estimated to be 13.4 mol.%. The fact that the bulk Co fraction is lower than that of the alloy stoichiometry is an initial indication of Co segregation.

The local environments of the Pt and Co atoms were further investigated using X-Ray Absorption Spectroscopy (XAS). Data processing was done using the program Athena of the Demeter suite. Catalyst samples were diluted with boron nitride and reduced at 250 °C (pre-treatment temperature) and 400 °C (higher than the pretreatment temperature) for 1 h (ramp rate 5 °C min<sup>-1</sup>) under atmospheric pressure in a 40 ml min<sup>-1</sup> hydrogen flow prior to measurement at ambient temperature under hydrogen. On the Pt edge, the white line and edge positions of the alloy coincide with those of the Pt foil for both reduction temperatures, <sup>9</sup> demonstrating that the Pt is fully reduced in all cases. However, the Extended X-Ray Absorption Fine Structure (EXAFS) on the Pt edge<sup>9</sup> suggests that there is surface segregation of Co in the Pt-Co alloy particles, as the Pt:Co ratio in the Pt coordination sphere ( $3.1 \pm 0.6$ ) is greater than the nominal. Considering the fact that the cobalt precursor was injected at 170 °C in the synthesis, it is reasonable that the Pt-Co alloy NCs had cobalt rich shell, because platinum precursor can be decomposed and nucleated at lower temperature, which

possibly formed the core of NCs. After reduction at 400°C, the Pt:Co ratio in the Pt coordination sphere is closer to the nominal  $(2.1 \pm 0.4)$ , consistent with at least partial reverse Co segregation to the bulk. A similar reverse segregation phenomenon has been reported previously for PtNi nanoparticles<sup>242</sup>.

The X-Ray Absorption Near Edge Spectra (XANES) of the Co K edge<sup>9</sup> provides further information on the nature of the alloy NCs. First, the spectra indicate that Co remains partially oxidized, even after reduction at 400°C. Using a linear combination of spectra from CoO and Co standards to fit the results for the alloy catalyst, the average Co oxidation states after reduction at 250°C and 400 °C were 1.2 (60% CoO) and 0.72 (36% CoO), respectively. Surface oxygen is known to induce Co surface segregation in a Pt-Co alloy<sup>243</sup>. In turn, Co forms a surface monolayer oxide with properties distinct from those of the bulk CoO<sup>244</sup>. In order to determine the most likely surface/catalytic site structure that would be consistent with all experimental data, we employed a data-driven theoretical modeling approach developed in the next section.

# 5.5.2 Data-driven Theoretical Catalyst Model

# 5.5.2.1 Approach and Approximations

The feasibility of our modeling approach hinges on the unique catalyst synthesis procedure, which resulted in PtCo NCs with uniform size and composition. Scheme 2 summarizes experimental characterization data categories utilized in structure elucidation. First, we hypothesize the NC structure, consistent with experimental constraints, such as the TEM-based nanoparticle diameter and the ICPbased nominal Pt:Co ratio. Then we employ our mean-field-type model (Section 5.5.2.2) to calculate average Pt-Pt and Pt-Co coordination numbers, Co oxidation state, and the bulk Pt:Co ratio. Finally, we assess the credibility of the hypothesized structure through comparison with XAS-derived coordination numbers and oxidation states and XRD-derived bulk Pt:Co ratios.



Scheme 2. Data flow for determination of a realistic NC model.

As step sites constitute ca. 30% of all surface sites for 3-4 nm nanoparticles<sup>245</sup> and tend to stay more oxidized than terraces<sup>246</sup>, we assume 30% of surface sites to be composed of Co in the +2 oxidation state. Following an analogous Fe<sub>3</sub>O<sub>2</sub>/Pt(111) structure observed using STM<sup>247</sup>, we consider the rest of the monolayer surface oxide to be Co<sub>3</sub>O<sub>2</sub> with a honeycomb structure on a Pt-Co metallic core as a nanoparticle model (Figure 5.5a). The local atomic surface environment is assumed to be identical to that of the DFT-optimized Co<sub>3</sub>O<sub>2</sub>/Pt(111).



Figure 5.5. (a)  $Pt_3Co_2$  nanocrystal model involving an alloy core (88% Pt, 12% Co based on XRD) covered with a  $Co_3O_2$  surface oxide monolayer with a honeycomb structure; (b) and (c) correspond to Pt and  $Pt_3Co$  NC models.

# 5.5.2.2 Calculation of Coordination Numbers

We estimate average Pt coordination numbers of a core/shell nanoparticle for comparison with XAS results according to the following equation:

$$CN_{av} = x_{bulk} \times CN_{bulk} + x_{subsurf,step} \times CN_{subsurf,step} + x_{subsurf,ter} \times CN_{subsurf,ter}$$

Here  $CN_{av}$  is the average coordination number (Pt-Co or Pt-Pt);  $CN_{bulk}$ ,  $CN_{subsurf,step}$ , and  $CN_{subsurf,ter}$  are coordination numbers in the bulk and the subsurface layer under a step site and under a terrace, respectively; and x is the corresponding fraction of atoms of a given type (Co or Pt). We compute  $CN_{bulk}$  as

$$CN_{bulk,i} = 12 \times y_i$$

Here 12 is a total coordination number in the bulk;  $y_i$  is the bulk fraction of a metal i (Pt or Co), as found from the overall nanoparticle composition, minus the number of surface Co atoms (see below). In the subsurface layer under a terrace, metal atoms are in contact with the core Pt-Co alloy (total coordination number 9 for an ideal Co<sub>3</sub>O<sub>2</sub>/Pt(111) structure) and the Co<sub>3</sub>O<sub>2</sub> surface oxide layer on top. Accordingly, the CNs are calculated as

$$CN_{subsurf,Pt-Pt,ter} = 9 \times y_{Pt};$$
  
$$CN_{subsurf,Pt-Co,ter} = 9 \times y_{Co} + \frac{1}{4} \times 3 + \frac{3}{4} \times 2$$

The factors 1/4 and 3/4 reflect the fact that among every 4 atoms in a subsurface layer of a (4x4) supercell, one is bound to 3 Co atoms and three to 2 Co atoms of a surface oxide. The sublayer CNs under step sites are calculated assuming a Pt(211) geometry, as

$$CN_{subsurf,Pt-Pt,step} = 7 \times y_{Pt};$$
$$CN_{subsurf,Pt-Co,step} = 7 \times y_{Co} + 5$$

Here 7 and 5 are the numbers of non-surface and surface neighbors, respectively.

We estimate the fraction of Pt and Co atoms in each layer by approximating the nanoparticle as a sphere, taking advantage of the fact that EXAFS data are insensitive to the actual NC shape in the 3-4 nm diameter range. The total number of atoms is calculated by dividing the particle volume by the volume of a primitive unit cell (dimensions using the XRD-based lattice constant). For a Pt<sub>3</sub>Co<sub>2</sub> NC with a 3.7 nm diameter, the number of atoms equals 1827. The number of surface atoms is computed by dividing the particle surface area by a per-atom area in a Pt(111) (4x4) supercell with dimensions corresponding to the Pt<sub>3</sub>Co<sub>2</sub> lattice constant. Accordingly, we find the 3.7 nm-particle dispersion to be 36%, close to values obtained with a different method<sup>248</sup>. The number of atoms in the subsurface layer was calculated in a similar fashion using a nanoparticle of the actual radius minus the distance between subsurface and surface layers (2.041 Å, as in the  $Co_3O_2/Pt(111)$  slab). To obtain the total number of surface Co atoms, we scale the number of 70% of surface sites by a factor of 12/16 to reflect the fact that every 12 Co atoms in a  $Co_3O_2$  honeycomb geometry occupy area equivalent to 16 surface Co (or Pt) atoms in a close-packed configuration. We assume the number of sublayer atoms under step sites to be equal to the number of step sites.

Results of model-based calculations for Pt NCs, Pt<sub>3</sub>Co<sub>2</sub> random and core-shell alloys are given in Tables D.1 and D.3.

### 5.5.2.3 Comparison with Experiment

Table 5.1 compares XAS/XRD results with geometric estimates of the alloy core/oxide shell spherical nanoparticle model. Overall, the model exhibits excellent agreement with our experimental data, particularly given the approximations invoked. We predict an average Co oxidation state of 1.18, close to the experimental estimated value of 1.20. The low Co oxidation state is consistent with an O:Co atomic ratio of less than 1 on the majority of surface sites. In contrast, a previously observed surface oxide with CoO stoichiometry<sup>244</sup> would yield an average oxidation state >1.5, different from the XANES results. The predicted Co content in the bulk alloy (14.4 mol. %) is close to the Vegard's law estimation from XRD (13.4 mol. %) The experimental and geometric Pt-Co and Pt-Pt CNs agree well. The XAS data demonstrate that  $Pt_3Co_2$  NCs, reduced at 250°C, consist of a Pt-rich core with the majority of Co segregated to the surface, forming a CoO<sub>x</sub> surface oxide shell. The

 $Co_3O_2$  honeycomb monolayer as a dominant surface structure is consistent with XAS results.

Table 5.1. Average coordination numbers and Co oxidation states for  $Pt_3Co_2$  NCs reduced at 250°C, determined by X-ray absorption spectroscopy and estimated using a spherical core/shell NC model with planes covered by a  $Co_3O_2$  surface oxide monolayer (70%) and step sites covered by CoO (30%). CN stands for "coordination number".

	XAS/XRD data	Geometric Model
Co oxidation state	$1.20^{1}$	1.18
Pt-Co CN	$2.88^1 \pm 0.44$	2.92
Pt-Pt CN	$8.98^{1}\pm0.57$	8.91
Co content in the bulk alloy, %	13.4 <sup>2</sup>	14.4

<sup>1</sup>XAS data regression; <sup>2</sup>XRD analysis (Vegard's law)

Further evidence for Co<sub>3</sub>O<sub>2</sub> surface oxide formation comes from CO chemisorption measurements on NCs supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>9</sup> After reduction at 250°C, CO adsorption on the Pt<sub>3</sub>Co<sub>2</sub> NCs is negligible, consistent with the Pt atoms being covered. After 400°C reduction, CO chemisorption is comparable to what was observed with Pt NCs, due to reverse segregation of Co to the bulk. DFT results indicate that CO interacts weakly with Co<sub>3</sub>O<sub>2</sub>/Pt(111) compared to Pt(111) (ca -0.7 vs. ~-2 eV electronic binding energy<sup>247</sup>, respectively), consistent with the lack of CO adsorption. A similar in magnitude CO binding energy was correlated with no CO adsorption in XPS measurements on Fe<sub>3</sub>O<sub>2</sub>/Pt(111) honeycomb structure<sup>247</sup>. The importance of a Co<sub>3</sub>O<sub>2</sub> overlayer structure is further supported from DFT calculations, discussed next.

# 5.5.3 Theoretical Insights into the Reaction Mechanism, Catalyst Composition Effects, and Catalyst Stability

DFT calculations were performed in order to understand the mechanism of the HDO reaction, catalyst stability issues, and the differences among the three catalysts (Pt, Pt<sub>3</sub>Co, and Pt<sub>3</sub>Co<sub>2</sub>). Regarding the reaction mechanism on the Pt<sub>3</sub>Co<sub>2</sub> catalyst, the calculations showed that the Co<sub>3</sub>O<sub>2</sub> honeycomb monolayer supported on the Pt rich core is capable of catalyzing key reaction steps involved in the HMF to DMF conversion. The overall reaction is assumed to proceed via the following steps: 1) H<sub>2</sub> dissociation, 2) C=O hydrogenation, and 3) selective HDO with concomitant oxygen removal from the surface in the form of water. These steps and their activation barriers are reported in Table D.2.

The H<sub>2</sub> dissociation step can occur via several homolytic and heterolytic dissociation paths (Table D.2). The calculations indicate that homolytic splitting of a weakly physisorbed H<sub>2</sub> molecule (-0.1 eV binding energy) over a single Co atom is most energetically favorable (a 0.7 eV reaction barrier). The final state (0.3 eV more stable than gaseous H<sub>2</sub>) entails both H atoms bound to Co and Pt atoms in bridging configurations (Figure D.1, reaction 1, transition state).

Prior to the C=O hydrogenation step, HMF weakly adsorbs on the surface (-0.8 eV BE); hydrogenation of the C=O carbonyl group exhibits a low reaction barrier when it is weakly bound to the surface.<sup>249,250</sup> Specifically, a concerted addition of two H atoms to HMF occurs with a 0.8 eV barrier, yielding BHMF. The overall hydrogenation is exothermic (reaction energy of -0.6 eV). BHMF can either desorb (0.9 eV desorption energy) or undergo HDO, ultimately forming DMF.

The subsequent HDO mechanism of BHMF on the Pt-rich particle with  $Co_3O_2$  coating is radical in nature, and is depicted in Figure 5.6 (Table D.2, reactions 7-10).

Some of us have found a similar mechanism of furfural HDO to form 2-methyl furan on a Ru/RuO<sub>2</sub> catalyst to be consistent with a range of experimental and computational data.<sup>8</sup> BHMF undergoes C-O bond scission on a honeycomb edge site consisting of two Co atoms (Figure D.1), forming a loosely bound radical and an OH group, with a reaction energy of +0.9 eV and a barrier of 1.2 eV. Next, a hydrogen atom transfers from the OH to the radical, yielding HMMF and a chemisorbed oxygen atom. C-O scission occurs similarly on the second hydroxymethyl group (not shown), forming DMF as the final product. The chemisorbed O atom (+1.7 eV binding energy with respect to H<sub>2</sub> and H<sub>2</sub>O) reacts rapidly with H<sub>2</sub> (a -1.2 eV exothermic dissociative adsorption with a 0.3 eV barrier) to form co-adsorbed OH and H that subsequently recombine with a 0.2 eV barrier (-0.9 eV reaction energy) to form water. Finally, water desorbs with a +0.4 eV energy to complete the catalytic cycle.



Figure 5.6. Reaction mechanism of BHMF hydrodeoxygenation to HMMF on the  $Co_3O_2/Pt(111)$  surface. DFT reaction barriers (energies) are given in eV. The inset depicts a portion of a  $Co_3O_2/Pt(111)$  surface. Two Co atoms participating in C-O bond activation are encircled with a white ellipsoid.

HMF, BHMF, HMMF, and DMF weakly interact with the  $Co_3O_2$  surface (~ - 0.8 eV BE, dominated by dispersion forces<sup>251</sup>, as opposed to chemisorption on metal atoms with BE of the order of -2 eV<sup>5</sup>), largely retaining a gaseous-like molecular geometry (Figure D.1). The absence of covalent bonding of the ring with the metal surface is key to rationalizing the high selectivity of the catalyst, because opening of the furanic ring and decarbonylation require strong chemisorption of the furan ring in

a flat geometry, with partial  $sp^2 \rightarrow sp^3$  re-hybridization of ring carbon atoms. <sup>50,79,158,252-</sup> <sup>254</sup> Lack of covalent bonding between the ring with the Co<sub>3</sub>O<sub>2</sub> oxide protects the ring from further side reactions and explains the low reactivity of DMF. The Co<sub>3</sub>O<sub>2</sub> surface layer is capable of catalyzing C-O bond hydrogenolysis in HMF that leads to selective production of DMF.

In order to assess the catalyst stability at a H<sub>2</sub>-rich environment, we calculated the rate of initiation of  $Co_3O_2$  reduction via vacancy formation, with the details presented in Section D.1. Under experimental HDO conditions (160°C, 33 bar H<sub>2</sub>), the vacancy formation rate is a factor of 2 lower than under *in situ* XAS conditions (250°C, 1 bar H<sub>2</sub>). Furthermore, the vacancy, once formed, is easily reoxidized by BHMF-to-HMMF reactions. This analysis provides a rationalization as to why the  $Co_3O_2$  surface oxide is stable in a reducing reaction environment.

In contrast to the highly selective, oxide-covered Pt<sub>3</sub>Co<sub>2</sub> catalyst, Pt carries out facile hydrogenation of the C=O group to BHMF, but dehydroxylates BHMF to form DMF slowly. <sup>9</sup> Furthermore, the DMF ring interacts strongly with Pt, promoting ring hydrogenation and ring opening with barriers which are lower than that of the dehydroxylation reaction. <sup>9</sup> The computed barriers for HDO of HMF are comparable to the barriers for ring hydrogenation and ring opening of DMF, consistent with the observation that selectivity to DMF is modest. <sup>9</sup>

Pt<sub>3</sub>Co NCs exhibit catalytic properties intermediate between Pt and Pt<sub>3</sub>Co<sub>2</sub>. Unlike the Pt<sub>3</sub>Co<sub>2</sub> NCs, there are not enough Co atoms to completely cover the surface with an oxide monolayer (Table D.3); in this catalyst, the surface is predicted to consist of 1/2 Co oxide and ~1/2 Pt atoms. We believe that this significant difference in structure exposes Pt patches on the surface (Figure 5.5b). The presence of Pt sites at the surface leads to the partial non-selectivity of the  $Pt_3Co$  catalyst.

# 5.6 Discussion

The development of better catalysts for HDO of HMF requires an understanding of the reaction mechanism. First, it is important to recognize that the reaction is sequential.<sup>173,240</sup> The poor selectivity that is observed with many metals is due to the fact that they further catalyze reactions of DMF, the desired product. While it is required that a catalyst has good activity for HDO of HMF, a selective catalyst must also be a poor catalyst for reactions of DMF. The sequential nature of the reaction also makes it essential that no part of the catalyst is nonselective. For reactions in which both the desired and side products form in parallel, having a small percentage of the catalyst surface showing a lower selectivity will not dramatically change the overall selectivity. With a sequential reaction, the nonselective part of the catalyst can have a much more dramatic effect.

This has important consequences for alloy catalysts. While the catalyst based on  $Pt_3Co_2$  NCs has the necessary properties to achieve very high selectivities, alloy catalysts prepared by conventional impregnation methods will not be so compositionally uniform. Both Pt and Co are individually are nonselective because they are active for reactions of DMF, so that any metal in the catalyst which is not in the form of an alloy will be nonselective.

In this context, it is interesting to consider the work from Schüth and coworkers<sup>234</sup>, who first reported extremely high selectivities for HDO of HMF with PtCo alloys. In their case, the highest selectivities were achieved when the metal particles were encapsulated in porous carbon spheres. We suggest that those carbon spheres were important for achieving a high compositional uniformity in the particles.

Catalyst stability is equally important to activity and our results suggest that there is a direct correlation between stability and selectivity. The most serious and rapid deactivation in our experiments was due to coking which must be caused by further reaction of overhydrogenated products, such as the 2,5-hexanedione. The Pt-Co alloy catalyst also seems to be more tolerant against sintering, possibly as a result of the core-shell structure.

# 5.7 Conclusions

High selectivity of DMF from liquid-phase HDO of HMF with H<sub>2</sub> can be achieved over a well-controlled Pt-Co/C catalyst. Particularly, over Pt<sub>3</sub>Co<sub>2</sub> catalyst, 98% of DMF yield was obtained with the optimized reaction temperature and space time. Recognizing the sequential nature of the HMF HDO reaction is the key for catalyst-development strategies. Noble metals interact strongly with the ring to promote side reactions. The fundamental principle for the superior performance of Pt<sub>3</sub>Co<sub>2</sub> is that the bimetallic alloy forms a monolayer oxide on the surface of the metallic core that interacts weakly with the furan ring to prevent over-hydrogenation and ring opening of DMF to secondary by-products while forming active sites to carry out the HDO process. In this regard, composition control is crucial to cover the entire surface with an oxide layer and avoid exposed metallic patches that can promote side reactions. Given that HDO is commonly employed in biomass upgrade, the learnings from this study could be used for the upgrade of other molecules, including bio-oil.

### Chapter 6

# FROM SCHRODINGER TO DFT: EVOLUTION OF QUANTUM MECHANICAL METHODS

# 6.1 Introduction

The main purpose of this Chapter is to expose the reader to key ideas and methods of quantum mechanics. It provides the context for a new quantum mechanical method, introduced in Chapter 7. Serving as a literature review, the Chapter aims to describe the field in as logically coherent manner as possible. It also differs from previously published reviews on density functional theory by a "problem-driven" exposition, as viewed through the lens of an engineer. First subsections are largely based on the author's personal interpretation of ideas expressed in the books of Landau and Lifshitz,<sup>255</sup> Szabo and Ostlund,<sup>256</sup> and Parr and Yang.<sup>257</sup>

### 6.2 Basics of Quantum Mechanics

In the early 20<sup>th</sup> century, there has been growing experimental evidence that the laws of classic mechanics are unable to explain phenomena involving subatomic particles – electrons and photons. For example, it has been observed that an electron exhibits a wave-particle duality, such that it acts as a particle upon photon-induced ejection (photoelectric effect), while also behaving as a wave in electron diffraction. Since the properties of waves are fully described by solutions of the wave equation, it was hypothesized and later inferred experimentally that the so-called wave function  $\Psi$  determines all properties of a system of N electrons (or any other quantum mechanical particles) in the current and all subsequent time instants:

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Psi(q) \tag{6.1}$$

Here  $\mathbf{r}_i$  is a displacement vector for a particle i, and q is a shorthand notation for a point in a so-called configurational space.

In classical mechanics, coordinates of a particle change continuously with time, i.e., there exists a path of a particle, meaning that both x(t) and  $\frac{dx}{dt}$  (velocity or momentum) exist and can be measured simultaneously. The two quantities x and  $\frac{dx}{dt}$  completely determine the state of a 1-particle, 1-dimensional system at time instant  $t_0$ , and represent sufficient information to make predictions about the mechanical system at an arbitrary time instant t with complete certainty. In quantum mechanics, however, the aforementioned phenomenon of electron diffraction unveils the non-existence of an electron path, and thus our inability to simultaneously measure x(t) and  $\frac{dx}{dt}$  (Heisenberg uncertainty principle, discovered in 1927). A fewer number of variables (1 instead of 2) specify a quantum mechanical state, indicating that predictions in quantum mechanics are probabilistic, rather than deterministic, in nature. Consequently, the goal of quantum mechanics is to predict *probabilities* of various measurements at t, provided that the state of a system at  $t_0$  is known.

The most straightforward property directly related to classical spatial wave amplitude is the wave intensity  $|\Psi(q)|^2 = \Psi(q)^*\Psi(q)$ . Since it is a positive quantity and is a function of coordinates, it is associated with the *probability* of finding a particle at a given coordinate q in the Born interpretation of quantum mechanics (1926). Consequently, the wave function should be normalized to yield the total probability of unity:

$$\int |\Psi(q)|^2 dq = 1 \tag{6.2}$$

The Born interpretation can be generalized by stating that probabilities associated with values of any system-inherent quantity (not just coordinates) are determined by expressions bilinear in  $\Psi$  and  $\Psi^*$ . From this statement the basic machinery of quantum mechanics follows.

In classical mechanics, waves are often superpositions of so-called normal modes having specific frequencies and energies. By analogy, we can formulate the principle of superposition in quantum mechanics: if measurements of the state  $\Psi(q)$  lead to results 1, 2, ..., i, ... and a measurement of a state  $\Psi_i(q)$  lead to the result i with certainty, then  $\Psi(q)$  can be expressed as a linear combination of states  $\Psi_i(q)$ :

$$\Psi(q) = \sum_{i} a_i \Psi_i(q) \tag{6.3}$$

From the probability bilinearity and the superposition principle, it follows that probabilities of values  $f_n$  of a measured quantity f equal  $|a_i|^2$ . Evidently,  $\sum_i |a_i|^2 = 1$ . Extraction of  $a_i$  from  $\Psi$  and  $\Psi_i$  is enabled by a standard trick, originally developed in the context of the Fourier transform and herein referred to as the "sandwich integration" trick – (6.3) is multiplied by a complex conjugate  $\Psi^*$ , expanded in  $\Psi_i^*$ , and integrated over q. Consequently,

$$a_i = \int \Psi_i^* \Psi \, \mathrm{dq} \tag{6.4}$$

Once  $a_i$  is known and thus the probabilities of finding various values of f, its average value is determined as:

$$\bar{f} = \sum_{i} |a_i|^2 f_i = \int \Psi^* (\sum_{i} a_i f_i \Psi_i) dq$$
(6.5)

The similarity of the expression in parentheses to (6.3) prompts us to define an operator  $\hat{f}$ , such that

$$\hat{f}\Psi = \sum_{i} a_{i} f_{i} \Psi_{i} \tag{6.6}$$

With this definition,  $\overline{f}$  can be expressed as the following:

$$\bar{f} = \int \Psi^* \hat{f} \Psi \, dq = \left\langle \Psi | \hat{f} | \Psi \right\rangle \tag{6.7}$$

Here the second equality defines the standard "bra-ket" notation. From (6.7) it follows that an operator corresponds to every measurable quantity. By choosing  $\Psi = \Psi_i$  in (6.6), one finds that the allowable values of a quantity f and its corresponding wave functions are the solutions to an eigenvalue problem:

$$\hat{f}\Psi = f\Psi \tag{6.8}$$

By considering the energy as f and solving the equation, one can find the lowest energy (ground state) of atoms, molecules, and solids, which is relevant to thermochemical reactions. Consequently, one should be able to make predictions about reaction rates, catalyst performance, etc. To do so, however, an expression for the operator that corresponds to energy needs to be derived.

From (6.8) it follows that, if two quantities f and g are simultaneously measurable, their operators commute:

$$\hat{f}\hat{g} - \hat{g}\hat{f} = 0 \tag{6.9}$$

By analogy with classical mechanics, the knowledge of a wave function at a certain time completely determines system dynamics. Mathematically, this can be stated as

$$i\hbar\frac{\partial\Psi}{\partial t} = \widehat{H}\Psi \tag{6.10}$$

In order to determine the source of the  $i\hbar$  prefactor and the physical quantity the operator  $\hat{H}$  corresponds to, one employs the correspondence between classical mechanics and quantum mechanics. By analogy with classical mechanics, which describes geometric optics as a limiting case of wave optics, we can recognize equivalence between the principle of least action and Fermat's principle and argue that in the (quasi) classical case the wave function reduces to the following form:<sup>255</sup>

$$\Psi = ae^{i\varphi} = ae^{\frac{iS}{\hbar}} \tag{6.11}$$

Here  $\varphi$  is a wave phase with large variations over space in comparison to a, *S* is the action, and  $\hbar$  is the Planck constant that relates the phase to the action. The passage to the quantum mechanical limit corresponds to  $\hbar \rightarrow 0$  in comparison to other quantities.

By substituting (6.11) into (6.10), one finds that in the classical limit, the  $\hat{H}$  eigenvalue corresponds to  $-\partial S/\partial t$ , which is the Hamilton function of the system in the Hamiltonian mechanics. The  $\hat{H}$  operator is correspondingly called Hamiltonian. It can be shown<sup>255</sup> that the Hamilton function is independent of time, and thus it is equivalent to energy.

The homogeneity of space manifests itself in the identical evolution of  $\Psi(q)$ and its parallelly displaced version  $\Psi(q + \delta q)$  with time according to (6.10), i.e., the parallel displacement has no effect on the Hamiltonian operator. After Taylor expansion  $\Psi(q + \delta q) = (1 + \delta q \nabla) \Psi(q)$ , one concludes that the  $\nabla$  operator commutes with  $\hat{H}$  according to (6.9) and thus its corresponding quantity can take definite values simultaneously with energy. The quantity that stems from space homogeneity is called *momentum*. If one defines an operator as  $\hat{p} = -i\hbar\nabla$  and determines its quasiclassical eigenvalues using (6.11),  $\nabla$ S will result, which is the classical momentum of the particle.

In classical mechanics, the total energy *E* is equal to the sum of the kinetic *T* and potential energy *V*, with  $T = \frac{p^2}{2m}$ . In quantum mechanics, since energy and momentum exist simultaneously, one can write  $T_i = \frac{p_i^2}{2m}$  and thus the kinetic energy operator as  $\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2$  or  $-\frac{1}{2} \nabla^2$  in atomic (dimensionless) units. Consequently, one obtains the eigenvalue problem for energy, first derived by Schrodinger in 1925:

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

$$\left(-\frac{1}{2}\nabla^{2} + \hat{V}\right)\Psi = E\Psi$$
(6.12)

Its generalization to the N-particle quantum mechanical system is straightforward and is described below.

#### 6.3 Hartree-Fock Approximation to the Schrodinger Equation

For atoms, molecules, and solids, containing negatively charged electrons and positively charged cores interacting with each other via Coulombic forces, the potential energy term in (6.12) can be expressed in terms of the electron-electron, electron-nuclei, and nuclei-nuclei interactions:

$$\widehat{H} = \widehat{T} + \widehat{V}_{Ne} + \widehat{V}_{ee} + \widehat{V}_{NN}$$
$$\widehat{H} = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \frac{1}{2M} \sum_{A} \nabla_{A}^{2} - \sum_{i} \sum_{A} \frac{Z_{A}}{r_{iA}} + \sum_{i} \sum_{j>i} \frac{1}{r_{ij}} + \sum_{A} \sum_{B>A} \frac{Z_{A}Z_{B}}{R_{AB}} \quad (6.13)$$

Here i and j indices correspond to electrons, and A and B – to nuclei; M is the ratio of masses of a nucleus and an electron; r and R are interelectronic and internuclear distances, respectively.

Due to the large difference between electronic and nuclear masses, the Born-Oppenheimer approximation commonly holds, stating that the motion of nuclei is decoupled from that of electrons and obeys laws of classical mechanics. The simplified Hamiltonian can be written in terms of electronic degrees of freedom as

$$\widehat{H} = -\frac{1}{2}\sum_{i} \nabla_{i}^{2} + \sum_{i} \nu(\mathbf{r}_{i}) + \sum_{i} \sum_{j>i} \frac{1}{r_{ij}}$$
(6.14)

Here  $v(\mathbf{r}_i) = -\sum_i \sum_A \frac{Z_A}{r_{iA}}$  denotes an external potential that electrons experience due to nuclei. If  $\hat{H}$  corresponds to N interacting electrons, the wave function  $\Psi$  is a function of 3N coordinates.

The solution of the Schrodinger equation using the Hamiltonian of the form (6.14) will yield the lowest energy eigenvalue for a specific configuration of nuclei. For a different configuration, it will yield a different value. By repeating this procedure, one can obtain the energy as a function of nuclear coordinates, i.e., the potential energy surface. Consequently, it will yield information on energy barriers, reaction energies, vibrational frequencies, entropy, etc., and essentially any property relevant to chemistry. A natural strategy for solving the equation involves taking advantage of its linearity, which enables its recasting as a linear algebra problem.

The procedure begins with the superposition principle (6.3): the wave function is expressed as a superposition of "building blocks" (physical quantity eigenfunctions) – yet unspecified so-called basis set functions forming a complete set. For the wave function of 1 variable, this can be written as

$$\Phi(x_1) = \sum_i a_i \chi_i(x_1) \tag{6.15}$$

The  $\chi_i(x_1)$  functions, e.g., momentum eigenfunctions (plane waves), can make this decomposition equivalent to the Fourier transform, which is mathematically proven to be complete. Here  $a_i$  are constants to be optimized. For a function of 2 coordinates,  $a_i$ s become dependent on the second coordinate:

$$\Phi(x_1, x_2) = \sum_i a_i(x_2)\chi_i(x_1)$$
(6.16)

Proceeding further, one can expand each of  $a_i$ s in terms of the basis set using a new set of parameters  $b_{ij}$ :

$$a_i(x_2) = \sum_i b_{ij} \chi_j(x_2)$$
(6.17)

Combining (6.16) and (6.17), one obtains

$$\Phi(x_1, x_2) = \sum_{ij} b_{ij} \chi_i(x_1) \chi_j(x_2)$$
(6.18)

The wave function antisymmetry principle (6.19) reduces the number of free  $b_{ij}$  parameters and allows one to express the wave function as a linear combination of the so-called Slater determinants  $|\chi_i\chi_j\rangle$  (6.20).

$$\Phi(x_1, x_2) = -\Phi(x_2, x_1) \tag{6.19}$$

$$\Phi(x_1, x_2) = \sum_i \sum_{j>i} b_{ij} [\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)] = \sum_{i< j} 2^{\frac{1}{2}} b_{ij} |\chi_i\chi_j\rangle$$
(6.20)

Here the  $2^{\frac{1}{2}}$  factor arises due to the normalization requirement (6.2). After generalization of (6.20) to the system of N electrons and thus 3N coordinates, it

becomes clear that the number of parameters M required to define the wave function, grows exponentially:

$$M = p^{3N} \tag{6.21}$$

Here p is the number of parameters per degree of freedom. Remarkably, for a conservative estimate of p = 3 and N = 17 (the number of electrons in a chlorine atom), M exceeds the Avogadro number! Since application of linear algebra tools to solve the Schrodinger equation involves diagonalization of the MxM matrix, it is evident that the exact solution of the equation faces the "exponential wall" and is impossible to achieve, except for very small systems of no practical interest.

Fortunately, the "sandwich integration trick" (6.4) introduced above provides a way on how to proceed. If we apply it to the Schrodinger equation  $\hat{H}\Psi = E\Psi$  by multiplying it by variation  $\delta\Psi$  on the left and integrating, the so-called variational principle will result:

$$\delta(\langle \Psi | \hat{H} | \Psi \rangle - E \langle \Psi | \Psi \rangle) = 0 \tag{6.22}$$

The principle essentially reformulates the Schrodinger equation as a solution to a constrained minimization problem, where E plays a role of a Lagrange multiplier. Its consequence is that, if one uses approximations to the wave function, first-order errors in it will lead to second order errors in energy, and thus one may hope that even approximate wave functions will provide reasonable energy estimates.

The natural (and simplest) approximation to (6.20) is to eliminate the dependence of the number of terms on the system size and retain only one term (6.23):

$$\widetilde{\Phi}(x_1, x_2) = |\chi_1 \chi_2\rangle \tag{6.23}$$
By applying the variational principle to the wave function of the form (6.23) and expanding  $\chi_i$  in a standard basis set (e.g., atomic orbitals or plane waves), one finds that  $\chi_i s$  are solutions to Schrodinger-like equations, called Hartree-Fock (HF) equations (introduced in 1927 and 1930), describing a motion of a single electron in an effective potential field (mean field)  $v_{eff}$  due to all other electrons:

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}\right]\chi_i = e_i\chi_i \tag{6.24}$$

The HF approximation reduces the original intractable N-body problem to N 1body problems. The total energy can be determined by substituting  $\tilde{\Phi}$  (6.23) into (6.7) for the Hamiltonian (6.14), resulting in the following expression:

$$E_{HF} = \sum_{i} \left\langle \chi_{i} \left| -\frac{1}{2} \nabla^{2} \right| \chi_{i} \right\rangle + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + U[\rho] - \frac{1}{2} \sum_{i} \sum_{j} \left\langle \chi_{i} \chi_{j} \right| \chi_{j} \chi_{i} \right\rangle$$
(6.25)

Here the terms correspond to kinetic energy, classical electrostatic energy for interactions between nuclei and electrons, electron-electron interactions  $(U[\rho])$ , and the electron exchange energy due to antisymmetry requirement (6.19) (internuclear interaction term is omitted).  $\rho$  is the electron density, calculated as  $\rho = \sum_i |\chi_i|^2$ .  $v(\mathbf{r})$  is an external electrostatic potential due to nuclei. The  $U[\rho]$  electrostatic term has the following form:

$$U[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$
(6.26)

Since a squared wave function corresponds to the probability distribution of electrons in space, we will find that, in the HF approximation, the total probability distribution equals the product of 1-electron probabilities, i.e., motion of electrons is uncorrelated (independent particle approximation). Lack of electron correlation results

in energies of atoms and molecules being too high, as follows from the variational principle (6.22), significantly deviating from experimental values. To account for correlation, the pre-optimized HF orbitals  $\chi_i$  are employed in expansions of the type (6.20) (Configuration Interaction), which is, however, computationally prohibitive due to the exponential wall, except for very small systems. More practically, the correlation is taken care of in either perturbation theory (PT) or the coupled cluster (CC) theory, which are a means to systematically reduce the number of independent parameters in (6.20). HF, PT, and CC formally scale with the number of atoms as N<sup>4</sup>, N<sup>5</sup> and higher, or N<sup>6</sup> and higher, respectively, which limits the applicability of those methods to tens of atoms, making them unsuitable for problems in heterogeneous catalysis. To merely illustrate the complexity of the equations (this is needed for the subsequent discussion), in (6.27) we report the total energy as a sum of the HF energy (6.25) and the correlation energy, calculated using the 3<sup>rd</sup>-order PT. It should be noted that one typically has to go to even more complex and expensive 4<sup>th</sup>-order PT to obtain reasonable accuracy (e.g., atomization energies with a mean absolute error of  $2.6 \text{ kcal/mol}^{258}$ ).

$$E = E_{HF} + \frac{1}{4} \sum_{abrs} \frac{|\langle ab||rs \rangle|^2}{e_a + e_b - e_r - e_s}$$

$$+ \frac{1}{8} \sum_{abcdrs} \frac{\langle ab||rs \rangle \langle cd||ab \rangle \langle rs||cd \rangle}{(e_a + e_b - e_r - e_s)(e_c + e_d - e_r - e_s)}$$

$$+ \frac{1}{8} \sum_{abrstu} \frac{\langle ab||rs \rangle \langle rs||tu \rangle \langle tu||ab \rangle}{(e_a + e_b - e_r - e_s)(e_a + e_b - e_t - e_u)}$$

$$+ \sum_{abcrst} \frac{\langle ab||rs \rangle \langle cs||tb \rangle \langle rt||ac \rangle}{(e_a + e_b - e_r - e_s)(e_a + e_c - e_r - e_t)}$$
(6.27)

The reason why HF, and especially PT and CC methods, are so expensive is the large number of terms representing interactions of multiple electron configurations that they involve. Since physical quantities in quantum mechanics are described by definite integrals (6.7), we can anticipate that statistical approaches that would effectively average out multiple interactions, should yield more tractable equations, enabling accurate QM calculations at much lower computational cost. This philosophy parallels that of statistical mechanics and thermodynamics: despite an order of Avogadro number of interacting molecules, equations linking emergent thermodynamic properties (energy, entropy, etc.) are relatively simple, and a single property of a system (radial distribution function) describes the thermodynamic state. Since PT and CC methods for obtaining correlation energy are built on top of HF and use HF orbitals, one can hope that by developing a statistical approximation to HF, correlation energy calculations will also be simplified in the new framework.

# 6.4 Density Functional Theory

The systematic development of a statistical approximation to HF begins with the recognition that classical mechanics is an approximation to the quantum mechanics with the asymptotic wave function (6.11) at  $\hbar \rightarrow 0$ . Moving away from the classical approximation while  $\hbar$  is still small relative to other quantities, one can expand *S* in Taylor series with respect to  $\hbar$ , resulting in a Wentzel–Kramers–Brillouin-Jeffreys (WKBJ) approximation, developed in 1926:<sup>255</sup>

$$\Psi = \operatorname{a} \exp\left(\frac{i}{\hbar} \left(\sigma_0 + \sigma_1 \frac{\hbar}{i} + \sigma_2 \left(\frac{\hbar}{i}\right)^2 + \sigma_3 \left(\frac{\hbar}{i}\right)^3 + \cdots\right)\right)$$
(6.28)

While retaining only the  $\sigma_0$  term corresponds to a purely classical case, which is too drastic an approximation due to chemical bonding and electron motion being non-classical phenomena, retaining both  $\sigma_0$  and  $\sigma_1$  provides a lot of promise. In particular, it provides a formal basis for the Born-Sommerfeld quantization rule in the old quantum theory, which was historically successful in describing the hydrogen emission spectrum. The rule associates a phase space volume  $(2\pi\hbar)^3$  with each quantum state  $\chi_i$ , effectively allowing one to treat a volume element dV as homogeneous electron gas and apply to it the simplest theoretical construction in quantum mechanics – the particle-in-a-box problem. The ultimate result is the energy expressed as a functional of the electron density (Thomas-Fermi-Dirac equation, TFD, developed in 1927; exchange term added by Dirac in 1930):

$$E[\rho] = C_F \int \rho(\mathbf{r})^{5/3} d\mathbf{r} + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + U[\rho] - C_x \int \rho(\mathbf{r})^{4/3} d\mathbf{r}$$
(6.29)

The term correspondence is analogous to (6.25).  $C_F$  and  $C_x$  are known constants.  $v(\mathbf{r})$  is the external electrostatic potential due to nuclei. While the method was surprisingly accurate for total energies of atoms, it was unable to describe atomic shell structure and the chemical bond formation.

Motivated by the astonishing simplicity and partial success of the Thomas-Fermi-Dirac theory, in 1964 Hohenberg and Kohn proved a theorem stating that the *exact* total energy (as opposed to the approximate one in (6.29)) of any interacting system of N electrons in the external potential of atomic nuclei is a unique functional of electron density  $E = E[\rho]$ .<sup>259</sup> The Density Functional Theory (DFT) was born. Their second theorem formulated the variational principle akin to (6.22): for a trial density  $\tilde{\rho}$  that integrates to N over space, the following inequality holds:

$$E_0 \le E[\hat{\rho}] \tag{6.30}$$

$$\delta E[\rho] = 0$$

The (6.30) allows one to determine the ground state  $E_0$  of the quantum mechanical system by finding the electron density distribution that minimizes the energy of the system, provided that the energy functional is known, i.e., to solve a constrained optimization problem. The total energy is expressed in terms of the kinetic energy functional  $T[\rho]$ , and the potential energy of electron-electron  $V_{ee}[\rho]$  and electron-nuclei interactions  $V_{Ne}[\rho]$ , with the former two terms combined to the Hohenberg-Kohn functional  $F_{HK}[\rho]$ , the exact form of which is unknown:

$$E[\rho] = T[\rho] + V_{Ne}[\rho] + V_{ee}[\rho] = \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{HK}[\rho]$$

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho]$$
(6.31)

The long-range classical electron-electron interaction term  $U[\rho]$  is customarily separated from  $V_{ee}[\rho]$ :

$$V_{ee}[\rho] = U[\rho] + G[\rho] \tag{6.32}$$

In comparison to the original Schrodinger equation (eq. (6.12) and (6.13)), which involves a transparent functional form, but a highly complex wave function of 3N variables, DFT employs a much more tractable electron density as a function of only 3 variables, but an obscure functional form.

One now faces a dilemma – on the one hand, there is the Hartree-Fock approximation that describes chemical bonding features correctly but is quite inaccurate. On the other hand, there is the exact density functional theory, which, however, yields an even more inaccurate, while very inexpensive Thomas-Fermi-Dirac approximation. Practically, the most systematic way to proceed and develop

approximations to the universal functional  $T[\rho] + G[\rho]$  is to take the best from both worlds, as was done by Kohn and Sham in 1965.<sup>260</sup>

The solution represents a common treatment of many-body effects that prevails in science: the energy of a complex, many-body system is expressed as a sum of the energy of a tractable system of independent particles (*reference system*) plus *corrections* due to interactions. For example, in thermodynamics, the Gibbs free energy of a mixture is expressed as a Gibbs free energy of an ideal mixture containing non-interacting particles, which is trivial to find, plus the excess Gibbs free energy, related to the concept of an activity coefficient. Similarly, the total energy of an interacting electron system can be expressed in terms of the energy of independent electrons  $E_{IE}[\rho]$  plus corrections due to exchange and correlation effects, termed as the exchange-correlation functional  $E_{xc}[n]$ :

$$E[\rho] = E_{IE}[\rho] + E_{xc}[\rho]$$

$$E_{IE}[\rho] = T_s[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2$$

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + G[\rho]$$
(6.33)

Here  $T_s[\rho]$  is the kinetic energy of independent electrons,  $\sum_i \langle \chi_i | -\frac{1}{2} \nabla^2 | \chi_i \rangle$ .

The Kohn-Sham theory can be deduced through a different line of reasoning, which we find helpful for the novel method development, described in the next chapter. After visual inspection of the 3<sup>rd</sup>-order PT expression (6.27), one may anticipate that any simpler, density-based equations will necessarily be approximations, akin to the Thomas-Fermi theory. This will amount to approximations of astronomical numbers of integrals, which have similar 4-orbital structure in both exchange and correlation terms. This similarity suggests that exchange and correlation

should be statistically approximated together to ensure maximum error-cancellation. Since the kinetic energy term has a totally different functional form and contains a relatively small number of integrals, it should be treated explicitly. Thus, we arrive at (6.33).

Application of the variational principle (6.30) leads to the well-known Kohn-Sham equations,<sup>260</sup> similar to HF (6.24), except that they are in principle exact, provided that  $E_{xc}[n]$  is known:

$$\left[-\frac{1}{2}\nabla^2 + \nu(\mathbf{r}) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + \frac{\delta E_{xc}[\rho]}{\delta\rho}\right] \chi_i = e_i \chi_i$$
(6.34)

Solution of Kohn-Sham equations proceeds as follows. First, an initial guess for the electron density distribution  $\rho_{in}$  is generated and used for evaluation of density-dependent terms in the brackets of (6.34). Next, the eigenvalue problem is solved and a set of delocalized orbitals  $\chi_i$  is obtained. Then the new electron density profile is generated from the occupied orbitals as  $\rho_{out} = \sum_i |\chi_i|^2$ . The sequence is repeated until self-consistency is achieved, i.e.,  $\rho_{out} = \rho_{in}$ .

## 6.5 Exchange-correlation Functionals

#### 6.5.1 Local Density Approximation (LDA)

The success of the Kohn-Sham scheme for making realistic descriptions of atom-based quantum mechanical systems critically depend on the knowledge of the sufficiently accurate exchange-correlation functional  $E_{xc}[\rho]$  (see (6.33)). The exchange-correlation functional accounts for two effects not captured by the independent particle approximation: (1) exchange due to forbidden occupation of the same point in space by two electrons having the same spin; and (2) correlation due to

the fact that repelling electrons tend to avoid each other, reducing their effective interaction energy. As we stated previously, the statistical approximation should be applied to exchange and correlation simultaneously.

The statistical theory of the exchange stems directly from the quasi-classical (WKBJ) approximation (6.28), when the  $\sigma_0$  and  $\sigma_1$  terms are retained. It takes the following functional form (compare with (6.29)):

$$E_{x}[\rho] = -0.7386 \int \rho(\mathbf{r})^{4/3} d\mathbf{r}$$
(6.35)

This expression is identical to that for the exact exchange energy of a homogeneous electron gas; since it involves electron density only at point **r**, it is referred to as the Local Density Approximation (LDA). The corresponding approximation for correlation effects, which would be consistent with LDA, employs exact correlation energy of electron gas, calculated using Quantum Monte Carlo at certain densities and interpolated according to Vosko, Wilk and Nusair (VWN).<sup>261</sup> The VWN expression is very complex; a simpler (and in fact more accurate) one has been recently derived based on the 2<sup>nd</sup>-order PT,<sup>262</sup> in which parameters a and b are evaluated from the high-density correlation energy limit and are thus not fitted:

$$E_{c}[\rho] = a \ln\left(1 + \frac{b}{r_{s}} + \frac{b}{r_{s}^{2}}\right); r_{s} = \left(\frac{3}{4\pi\rho}\right)^{1/3}$$
(6.36)

The LDA approximation is surprisingly accurate for molecular bond lengths (~0.02 Å MAE) and solid lattice constants and surface energies. However, it produces ~40 kcal/mol mean absolute atomization energy errors for molecules<sup>263</sup>, which made this method inapplicable to chemistry-related problems. Despite treating exchange and correlation only approximately, the method provides accuracy superior to the Hartree-

Fock method (~86 kcal/mol atomization energy errors) at only a fraction of computational cost.

The partial success of LDA can be attributed to the fact that the theory is exact for a real physical system (homogeneous gas) and thus it satisfies certain properties of the exact  $E_{xc}[\rho]$ . By recognizing that exchange-correlation effects correspond to reduction of the electrostatic interaction of electrons,  $E_{xc}[\rho]$  can be written in terms of the so-called exchange-correlation hole  $\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)$ , which quantifies electron density depletion at  $\mathbf{r}_2$  due to an electron at  $\mathbf{r}_1$ . The (6.37) describes the exchange part of  $E_{xc}[\rho]$  in terms of the exchange hole:

$$E_{x}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_{1})\rho_{x}(\mathbf{r}_{1},\mathbf{r}_{2})}{|\mathbf{r}_{1}-\mathbf{r}_{2}|} d\mathbf{r}_{1} d\mathbf{r}_{2}$$

$$(6.37)$$

The exact exchange hole satisfies the following criteria:<sup>264</sup>

$$\rho_{x}(\mathbf{r}, \mathbf{r}) = -\frac{\rho(\mathbf{r})}{2}$$

$$\rho_{x}(\mathbf{r}_{1}, \mathbf{r}_{2}) \leq 0$$

$$\int \rho_{x}(\mathbf{r}_{1}, \mathbf{r}_{2}) d\mathbf{r}_{2} = -1$$
(6.38)

The LDA exchange hole satisfies the same criteria. In addition, while exchange hole and correlation hole are separately non-local, their non-localities cancel each other out, making the local approximation to  $E_{xc}[\rho]$  quite reasonable. Taken together, these exchange-correlation hole properties explain the quite remarkable success of LDA and of the quasi-classical approximation (6.28) to the exchange-correlation energy functional in general.

#### 6.5.2 Generalized Gradient Approximation (GGA)

## 6.5.2.1 Concept

The systematic way to improve on the LDA exchange is to retain the  $\sigma_2$  (order- $\hbar^2$ ) term in addition to  $\sigma_0$  and  $\sigma_1$  in (6.28). While the quasiclassical wave function equation becomes considerably more complex,<sup>255</sup> one may recognize that corrections to energy involve the quantity  $\hbar p'/p^2$ , where p is the 1-particle momentum. The Fermi-level momentum (highest-energy electron in the system) is related to the Fermi wave vector  $k_F$  as  $p = k_F \hbar$ ; the latter is expressed in terms of electron density as  $k_F = (3\pi^2 \rho)^{1/3}$ . Taking it together, we find that order- $\hbar^2$  corrections to the semiclassical energy (and thus to LDA) should be expressed in terms of the so-called *generalized density gradient* (here a factor of 3 was replaced by a factor of 2 in line with the common convention due to Perdew<sup>265</sup>):

$$s(\mathbf{r}) = \frac{1}{2(3\pi^2)^{1/3}} \times \frac{|\nabla\rho|}{\rho^{4/3}}$$
(6.39)

Both electron density and its gradient are local properties; from coordinate scaling arguments, it follows that any *local* (or *semilocal* when the gradient is included) exchange energy is homogeneous of degree 4/3 in density,<sup>257</sup> and thus it should always have a functional form similar to LDA (6.35). Therefore, the only possible way to incorporate  $\nabla \rho$  information into  $E_x[\rho]$  is the following:

$$E_{xc,gga}[\rho] = \int \rho \,\epsilon_{xc}(\rho, \nabla \rho) \,d\mathbf{r} = -0.7386 \int F(s)\rho^{4/3} \,d\mathbf{r}$$
(6.40)

The F(s) is called the exchange enhancement factor. F = 1 makes (6.40) identical to LDA. Equation (6.40) constitutes the basis of the so-called *Generalized Gradient Approximation* (GGA). The GGA is the most widely used class of exchange-

correlation (XC) functionals in the scientific community today, especially in heterogeneous catalysis.

To identify the most optimal functional form of F(s), we loosely follow the ingenious approach due to Chachiyo and Chachiyo (2017).<sup>266</sup>

In a hydrogen atom, the exact exchange energy (which cancels out electron self-interaction energy) is

$$E_{ex} = -\int d^3 r \rho(r) \left[ e^{-2r} \left( -\frac{1}{2} \right) + (1 - e^{-2r}) \frac{1}{2r} \right]$$
(6.41)

Since the electron density profile in the H atom is  $\rho(r) = \frac{1}{\pi}e^{-2r}$ , (6.41) is homogeneous of degree 2 in density. The following modification makes it consistent with the GGA expression (6.40) of homogeneity degree 4/3:

$$E_{ex,\text{loc}} \approx -\int d^3 r \rho(r) \left[ A \times e^{-2r/3} \left( -\frac{1}{2} \right) + B \times \left( 1 - e^{-2r/3} \right) \frac{1}{2r} \right]$$
(6.42)

The 1/2r term in (6.42) is the exact asymptotic limit of the exchange energy density;  $e^{-2r/3}$  resembles a weighting function. It reaches the maximum value of 1 at r = 0. However, the generalized gradient  $s \propto e^{2r/3}$ , and thus it reaches the minimum value at r = 0. Therefore, (6.42) can be regarded as an interpolation between a slowly varying (homogeneous in a limit) electron gas and the exact  $s \to \infty$  limit:

$$E_{ex} = \int d^3 r \rho(\mathbf{r}) \left[ w(s) \varepsilon_{unif} + (1 - w(s)) \varepsilon_{asymp} \right]$$
(6.43)

Evidently  $w(s) \propto \frac{1}{s}$ . To make w(s) finite at all s, Chachiyo suggested  $w(s) = \frac{1}{ds+1}$ , consistent with both s = 0 and  $s \to \infty$  limits. It can be shown that  $F(s) = \frac{cs}{\ln s}$  in the large-s limit; to make it finite at s = 0,  $F(s) = \frac{cs}{\ln(cs+1)}$ . After rearrangement, the following remarkably simple expression results:

$$F(s) = \frac{dcs^2 + \ln(cs+1)}{(ds+1)\ln(cs+1)}$$
(6.44)

Parameters c and d are determined from asymptotic and slowly varying electron-gas limits, resulting in the following non-empirical expression for the exchange enhancement factor:

$$F(s) = \frac{3x^2 + \pi^2 \ln(x+1)}{(3x^2 + \pi^2)\ln(x+1)}; x = \frac{4}{9}\pi s$$
(6.45)

Quite remarkably, the new functional describes atomic exchange energies more accurately than established methods (PBE, MGGA\_MS2, SCAN, and B88), with an average error approaching 0.115%. The functional simplicity and accuracy are astounding; in fact, it probably represents the first-of-a-kind, fully non-empirical F(s)expression. Unlike this method, more common GGA functionals, while also termed non-empirical, still employ functional forms guided by experiments and/or by trialand-error to match asymptotic limits and constraints. We describe them below.

#### 6.5.2.2 Historical Development

The  $F(s) = 1 + \beta s^2$  functional form was the first gradient-based correction to LDA, introduced on dimensional grounds by Herman et al. in 1969.<sup>267</sup> In that historic period, it was termed the Gradient Expansion Approximation (GEA). Although fitting the  $\beta$  parameter to atomic exchange energies ( $\beta = 0.0022 \dots 0.0034$  a.u. as a function of Z) was found to provide accuracy superior to that of LDA,<sup>268</sup> explicit calculation of  $\beta = 0.001667$  a.u. from homogeneous gas properties was found to yield disastrous results, much worse than LDA.<sup>269</sup> Perdew realized that the poor GEA performance is a consequence of the fact that no physical system exists that is described by GEA exactly, and GEA violates the exact exchange hole conditions (6.38) (the so-called

sum rule).<sup>264</sup> The importance of sum rules has been demonstrated earlier by Becke in 1983, who derived the close-to-empirical  $\beta = 0.0029$  a.u. value by enforcing (6.38)  $(X\alpha\beta$  functional).<sup>268</sup> A class of gradient-based XC approximations, which satisfy necessary constraints, was termed as the "Generalized Gradient Approximation" (GGA).

Two key disadvantages of the  $F(s) = 1 + \beta s^2$  form are: (1)  $\beta$  is atomdependent and thus not universal, and (2) the exchange potential diverges at atomic density tails with  $s \to \infty$ . A follow-up quest for a more optimal F(s) functional form was driven by (1) empirical method performance for atoms, (2) asymptotic properties of the exact exchange functional, and (3) Occam's Razor.

Formally an extension of Becke's work, Perdew used a more sophisticated, first principles approach in GGA development and used GEA as a starting point, on which exchange hole sum rules (6.38) were imposed in the simplest possible manner through the use of Heaviside (step) functions.<sup>265</sup> In this way, both the exact homogeneous gas  $\beta$  value and sum rules were satisfied, an advantage over Becke's approach. The resulting complicated so-called "numerical GGA" reduced LDA exchange energy errors for spherical atoms from 14% for LDA to 1%.  $F^{GGA}(s)$  was then fitted by the following polynomial, resulting in the PW86 functional:

$$F^{PW86}(s) = \left(1 + \frac{0.0864s^2}{m} + bs^4 + cs^6\right)^m \tag{6.46}$$

PW86 represented a major milestone in the development of exchangecorrelation functional approximations.

In a separate semi-empirical development,<sup>270</sup> Becke eliminated the divergence problem of  $X\alpha\beta$  by introducing the simplest modification to  $F(s) = 1 + \beta s^2$ :

$$F^{B86}(s) = 1 + \frac{\beta s^2}{1 + \gamma s^2} = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa}}$$
(6.47)

Quite remarkably, a nearly unique choice of  $\beta = 0.0034 \dots 0.0038$  and  $\gamma = 0.004$  (for  $s = |\nabla \rho| / \rho^{4/3}$ ) yields almost exact exchange energies for atoms ranging from H to Xe, indicating that the functional form (referred to as  $X\alpha\beta\gamma$ , or B86, functional) is universal. This expression received further theoretical justification as an interpolation between small and large gradient limits.<sup>271</sup> In an attempt to reduce the number of empirical parameters from 2 to 1, Becke employed a known asymptotic behavior of exchange hole and electron density away from the nucleus (see Section 6.5.2.1), resulting in a widely acclaimed (~42,500 Google Scholar citations) B88 exchange functional (empirical  $\beta = 0.0042$ , if  $s = |\nabla \rho| / \rho^{4/3}$ ):<sup>272</sup>

$$F^{B88}(s) = 1 + \frac{\beta s^2}{1 + 6\beta s \sinh^{-1} s}$$
(6.48)

The B88 success demonstrated the power of a combination of empiricism and asymptotic criteria as a means to design optimal exchange functionals.

First-principles and semi-empirical GGA developments ultimately converged in the PW91 functional.<sup>273</sup> In comparison with PW86, the  $F_x(s)$  functional form (6.46) was replaced with the extended version of (6.48); real-space cutoff ideas and scaling criteria were extended to correlation energy functional, so that both exchange and correlation were treated consistently. The PW91 functional exhibited the remarkable performance in describing bonding in molecules and solids.<sup>273</sup>

The PW91 was designed to satisfy as many exact constraints as possible, resulting in a complicated, non-transparent functional form that was also overparameterized. It was realized that the GGA theory is too restrictive in general,

and thus a pragmatic approach is needed in choosing the most important constraints that the functional must obey. This approach has been used by Perdew, Burke, and Ernzerhof in the development of the PBE functional in 1996.<sup>14</sup>

The general-purpose PBE represented a major simplification over PW91 at the same level of performance. First of all, it employed Becke's transferable functional form (6.47), in which parameters were chosen in order to satisfy  $s \to 0$  and  $s \to \infty$ limits, rather than empirically. At  $s \rightarrow 0$  error cancellation between exchange and correlation was enforced, so that the exchange gradient contribution cancels that of correlation (known exactly), and the functional reproduces a homogeneous gas linear response. In the large-s limit, the parameters were chosen to satisfy the (local) Lieb-Oxford bound  $F_x(s) \le 1.804$  for many-electron systems.<sup>274</sup> It should be noted, however, that the (local) Lieb-Oxford bound is a controversial topic in the community and is hardly a necessary requirement, since it is naturally violated by the exact exchange in the tail of any finite system.<sup>275</sup> Nevertheless, a combination of nonempirical GGA exchange with GGA correlation functional, built using similar asymptotic principles, resulted in one of the most successful density functionals to date – PBE – with a never-ending list of applications in chemistry, condensed matter physics, and catalysis. The PBE article was cited >86,000 times as of July 2018 and was claimed the #16 most cited paper of all time in 2014.<sup>276</sup>

The well-known drawbacks of GGA methods in general and of PBE in particular include (1) overestimation of lattice constants, (2) too low predictions of metal surface energies (worse than LDA), (3) overbinding of adsorbates on metal surfaces, (4) too negative interaction energies between closed-shell atoms, and (5) lack of long-range correlations, responsible for van der Waals forces. Hereafter, analysis of methods to address #4 and #5 has been omitted; the following discussion focuses on the methods to improve description of strong metallic/covalent interactions that are relevant to catalysis. It has been realized that drawbacks 1-3 are due to the too restrictive PBE functional form, leading to the development of several specialized functionals.

As one example, it has been found that the slowly varying density limit of the enhancement factor  $F_x(s) = 1 + \mu s^2$  with  $\mu = 0.2195$  biases PBE toward more accurate description of atoms, as opposed to slowly varying density regions where atomic orbitals overlap, for which the  $\mu = 0.1235$  derived from GEA, is more appropriate. The corresponding  $\mu$  replacement with concomitant modification of the correlation part to fit surface energies of neutral jellium clusters resulted in the PBEsol functional (2008) that provided improved lattice constant and surface energy estimates, however, at the expense of reliable energy predictions.<sup>277</sup> We should note, however, that the method introduced in the next Chapter improves lattice constants without  $\mu$  modification, suggesting that this phenomenon is more complex.

The revPBE (1998) represents another example of a specialized PBE-derived functional, in which the  $\kappa$  value of 0.804 in (6.47) was replaced by 1.245 to fit exact atomic exchange energies, at the expense of the identical satisfaction of the local Lieb-Oxford bound.<sup>278</sup> revPBE improved atomization energies of molecules with multiple bonds and chemisorption energies, while worsening bond lengths and atomization energies of molecules with ordinary bonds.<sup>279</sup> The RPBE functional, designed by Hammer, Hansen, and Nørskov in 1999,<sup>280</sup> demonstrated a performance similar to that of revPBE, while satisfying the local Lieb-Oxford bound and being nonempirical in nature, which was achieved by the following modification of the enhancement factor:

$$F_{\chi}^{RPBE}(s) = 1 + \kappa \left(1 - e^{-\frac{\mu s^2}{\kappa}}\right)$$
(6.49)

Despite improved chemisorption energies, atomic exchange energies, and molecular atomization energies in comparison with PBE, RPBE further worsened surface energy predictions, equilibrium constants and unit cell volumes, as well as bulk moduli.<sup>281</sup> Moreover, a deeper analysis reveals<sup>282</sup> that RPBE is not so good for chemisorption too: if only molecules with single bonds are used as references, formation energy estimates for surface species are less accurate compared with PBE. Less optimal RPBE behavior is due to its key differences from PBE: (1) it does not correspond to the numerical GGA, developed by enforcing exchange hole sum rules, and (2) the  $F_x^{RPBE}(s)$  form is likely not as transferable as Becke's one (6.47), previously tested on atoms. Summing up, no specialized GGAs match PBE's performance, making it the most optimal starting point for further functional improvements. For this reason, PBE is used as a basis for the method developed in Chapter 6.

#### 6.5.3 Meta-GGA

Since the quasi-classical approximation to exchange-correlation energies (6.28) via retention of  $\sigma_0 + \sigma_1$  and  $\sigma_2$  terms has led to successful LDA and GGA, the natural extension is to include  $\sigma_3$ , equivalent to incorporating information on the density Laplacian into the exchange-correlation functional (6.50). Such (and related) methods are commonly referred to as meta-GGA functionals.

$$E_{xc}[\rho] = \int \rho \,\epsilon_{xc}(\rho, \nabla \rho, \nabla^2 \rho) \,d\mathbf{r}$$
(6.50)

To get a hint on the  $\nabla^2 \rho$  dependence, one can proceed following Becke<sup>268</sup> and express the exchange hole in (6.37) in terms of the finite displacement operator,<sup>255</sup> followed by spherical averaging and expansion in Taylor series ( $\mathbf{r} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}$ ;  $\mathbf{s} = \mathbf{r}_1 - \mathbf{r}_2$ ):

$$\rho_{x}(\mathbf{r}, \mathbf{r} + \mathbf{s}) = e^{\mathbf{s} \cdot \nabla_{1}} \rho_{x}(\mathbf{r}, \mathbf{r}_{1})|_{\mathbf{r}_{1} = \mathbf{r}} = \left(1 + \frac{1}{6}s^{2}\nabla_{1}^{2} + \cdots\right) \rho_{x}(\mathbf{r}, \mathbf{r}_{1})|_{\mathbf{r}_{1} = \mathbf{r}}$$
(6.51)

Finally,

$$\rho_x(\mathbf{r}, \mathbf{r} + \mathbf{s}) = \rho_x(\mathbf{r}, \mathbf{r}) + \frac{1}{6}s^2 \left(\nabla^2 \rho - 2\tau + \frac{1}{2}\frac{(\nabla\rho)^2}{\rho}\right) + \cdots$$
(6.52)

Here  $\tau = \sum |\nabla \varphi_i|^2$  is the kinetic energy density, and  $\varphi_i$  are Kohn-Sham orbitals. This expression demonstrates that, in addition to  $\nabla \rho$  and  $\nabla^2 \rho$ ,  $\tau$  also represents an important part of the exchange energy. In the original work, Becke assumed a semi-classical expansion of  $\tau$ :

$$\tau = \frac{3}{5} (6\pi^2)^{2/3} \rho^{5/3} + \frac{1}{3} \nabla^2 \rho + \frac{1}{36} \frac{(\nabla \rho)^2}{\rho} + \cdots$$
(6.53)

The (6.53) substitution into (6.52) ultimately led to Becke's  $X\alpha\beta$  functional, <sup>268</sup> described earlier. In a follow-up development,  $\tau$  was explicitly retained in (6.52), whereas a hydrogenic functional form of the exchange hole was assumed with one adjustable parameter to match the homogeneous gas limit, to yield encouraging results for atoms. However, the model performance for large-Z and small-Z was markedly different, necessitating further improvements.<sup>283</sup>

In a parallel line of thought, Bader<sup>284</sup> demonstrated that  $\nabla^2 \rho$  contains information on atomic shells, electron pairs, and bonding, which suggests that  $\nabla^2 \rho$ incorporation in (6.52) should lead to a more accurate exchange functional. However,  $\nabla^2 \rho$  was found to be insensitive to shell structure of heavy atoms, as well as diverge at atomic nuclei. At the same time, Becke extended the analysis above and introduced the electron localization function  $(ELF)^{285}$  involving conditional electron pair probabilities, expressed in terms of  $\tau$ -dependent dimensionless ratios (6.54).

$$a = \frac{\tau - \tau_W}{\tau_{unif}} \tag{6.54}$$

Here,  $\tau_W$  is the Weizsaker kinetic energy density, exact for any 1-electron orbital; and  $\tau_{unif}$  is that of the uniform electron gas. The *a* variable differentiates between absolutely localized 1-electron and 2-electron orbitals (covalent bonds; a =0), and delocalized, metal-like regions ( $a \approx 1$ ). Later it was recognized that the  $a \gg 1$ limit can account for weak interactions.<sup>286</sup> Due to such sensitivity, the idea to include  $\tau$  as a functional ingredient held a lot of promise to overcome the abovementioned GGA drawbacks, stemmed from the (6.40) functional-form limitations. Unlike  $\nabla^2 \rho$ , it does not blow up at nuclei and describes shell structure of heavy atoms well. The  $\nabla^2 \rho$ is related to  $\tau$  by expressions of the form (6.53), and thus (6.50) can be revised as follows:

$$E_{xc}[\rho] = \int \rho \,\epsilon_{xc}(\rho, \nabla \rho, \tau) \,d\mathbf{r}$$
(6.55)

Probably the most fruitful meta-GGA development has been led by Perdew and co-workers, who sought a non-empirical functional that would satisfy all known asymptotic and scaling conditions, while being a natural extension of PBE. Due to the importance of describing correctly the linear response in the slowly varying limit,<sup>14</sup> the second-order response treatment of the electron gas represented a logical starting point. Using the derivation for the slowly varying gas by Svendsen and von Barth,<sup>287</sup> Perdew and others<sup>288</sup> obtained the following enhancement factor expression in the slowly varying limit:

$$F_x^{response} = 1 + \frac{10}{81}s^2 + \frac{146}{2025}q^2 - \frac{73}{405}qs^2 + Ds^4 + O(\nabla^6)$$

$$s = C\frac{\nabla\rho}{\rho^{4/3}}; \ q = C\frac{\nabla^2\rho}{\rho^{5/3}}$$
(6.56)

To eliminate the diverging density Laplacian,  $\tilde{q}$  has been introduced such that in a slowly varying limit, it reduces to q in (6.56) by means of the kinetic energy density expansion (6.53):

$$\tilde{q} = \frac{9}{20}(a-1) + \frac{2s^2}{3}; \ a = \frac{\tau - \tau^W}{\tau^{unif}}$$
(6.57)

The enhancement-factor expression was taken to be similar to that of PBE:

$$F_{\chi}^{PKZB}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\chi}{\kappa}}$$
(6.58)

Here the  $x = x(s^2, \tilde{q})$  expression was constructed in a way that it recovers the exact linear response function (6.56) up to the 4<sup>th</sup> order.<sup>288</sup> As the D coefficient in (6.56) was initially unknown, it was subsequently fitted to molecular atomization energies. The correlation functional was based on that in PBE, except that kinetic energy density was employed to remove self-correlation error, based on prior work by Becke and others<sup>289</sup> (i.e., correlation energy for any 1-electron system should be zero). The resulting meta-GGA functional, termed PKZB (1999), demonstrated considerable error reduction for molecule atomization energies over PBE (3.1 vs. 7.9 kcal/mol), as well as surface energies and unit cell volumes, while providing rather mixed results for lattice constants,<sup>281,290</sup> and poor results for hydrogen-bonded complexes.<sup>291</sup>

Although the D parameter in (6.56) was originally fitted, its regressed value was found to differ from a numerical estimate,<sup>292</sup> introducing inconsistency into the theory. To improve over PKZB, Perdew and others<sup>293</sup> first recognized that larger bond

length errors in molecules than in solids, independent of the correlation functional choice, are indicative of incorrect large-gradient behavior of the exchange energy. This highlighted the necessity for the paradigm shift in functional development. All previous non-empirical LDA, GGA, and meta-GGA functionals were extrapolative in nature. They were based on properties of a nearly homogeneous electron gas and employed a semiempirical  $F_x(s)$  functional form to approach either the Lieb-Oxford (PBE) or the correct asymptotic exchange energy density limit (B88) at  $s \to \infty$ . Driven by PKZB failures, a new, interpolative approach was introduced by Perdew and co-workers<sup>293</sup> in the construction of the TPSS functional in 2006.

In TPSS, the  $F_x(s^2, \tilde{q})$  was chosen to satisfy both the uniform gas limit and a new paradigm system – the hydrogen atom, while obeying the Lieb-Oxford bound, making the exchange potential finite at the nucleus of 1- and 2-electron systems (exact constraint that is absent in GGA), and recovering the large *s* limit of PBE, relevant for weak bonding description. Obeying such diverse specifications required a highly complex functional form of *x* in (6.58). The PKZB correlation part was modified in order to restore the correlation energy dependence upon relative spin polarization at the low density limit of PBE, which was lost in PKZB. The very complex TPSS functional turned out to be very accurate for atomization energy, surface energy, and lattice constant estimates at computational cost comparable to GGA. Improvements over PKZB in lattice constants and hydrogen bond description were clear. However, the TPSS was less successful for molecules involving transition atoms, and especially alkali metal compounds.<sup>294</sup>

The TPSS form complexity provided multiple ways of how the TPSS performance can be improved. In one case, a constant controlling the way  $F_x(s^2, \tilde{q})$ 

approaches the large *s* limit was empirically modified, resulting in atomization energy MAE reduction from 5.81 to 3.79 kcal/mol for the G3/99 set of 223 molecules,<sup>295</sup> with minor improvement of reaction barriers. The revTPSS<sup>296</sup> (2009) involved further empirical modification of the functional form, as well as of large-*s* exchange enhancement factor to make it similar to that of PBEsol. The functional consistently reduced the lattice constant and surface energy errors, while retaining the TPSS level of accuracy for energetics. Therefore, it was hoped that revTPSS will become the "workhorse" functional for condensed matter physics and quantum chemistry. However, revTPSS still overestimates the desorption energy for CO on metals as PBE does<sup>297</sup> and displays large errors in cohesive energies<sup>298</sup> and in critical pressures of structural phase transitions in solids.<sup>299</sup> Very surprisingly, while both TPSS and revTPSS were designed to describe the slowly varying density limit more accurately than PBE, their performance was found to be poorer for solids.

Limited success of highly complicated TPSS and revTPSS brought about another paradigm shift. All functionals discussed previously were built around the idea of having a single functional form for  $F_x(s, a)$  or  $F_x(s)$  that asymptotically approaches the homogeneous electron gas, H atom, Lied-Oxford bound, etc. The new idea was to interpolate not between asymptotic limits, but between functional forms, so that for each value of *s* and *a*,  $F_x(s, a)$  is a weighted sum of enhancement factors for physical systems. In the meta-GGA by Sun and co-workers (MGGA\_MS2), introduced in 2012,<sup>300</sup> the exchange enhancement factor is

$$F_{x}(s,a) = F_{x}(s,a=1) + f(a)[F_{x}(s,a=0) - F_{x}(s,a=1)]$$
(6.59)

Here  $F_x(s, a = 1)$  and  $F_x(s, a = 0)$  are exchange enhancement factors for slowly varying density and a single-orbital limit, respectively. Remarkably, the functional demonstrated comparable or better performance than revTPSS, despite much greater simplicity. The functional also satisfied tighter the Lieb-Oxford bound<sup>301</sup> and did not have the order-of-limits problem, unlike TPSS and revTPSS. The downside was the large flexibility in choosing the interpolation function f(a) and its parameters, which were constrained to jellium surface energies and a hydrogenic anion.

It was argued<sup>286</sup> that among 3 possible dimensionless forms involving kinetic energy density, only (6.54) is capable of differentiating 1-electron, metallic, and weak bonds, which is not surprising, given its rigorous physical basis, as demonstrated by Becke. <sup>285</sup> The superiority of MGGA\_MS2 was attributed to this fact.

The culmination of meta-GGA functional development was the SCAN functional by Perdew and co-workers, developed in 2015.<sup>302</sup> It is based on the interpolation scheme akin to (6.59), modified to satisfy all known exact constraints for exchange and correlation energies and potentials, while interpolating between a = 1 and a = 0 limits and extrapolating to  $a \gg 1$  to describe weak interactions. At a = 0 (1-electron case) the enhancement factor was constructed to satisfy the strongly tightened Lieb-Oxford bound  $F_x \leq 1.174$ ; the  $F_x$  functional form was designed to approach  $s^{-1/2}$  at large *s* for the correct non-uniform coordinate scaling, not satisfied by LDA, GGA, and previous meta-GGA functionals. Since there are infinitely many ways to obey constraints, the functional forms and parameters were chosen to satisfy appropriate norms – uniform electron gas (as previous functionals did), jellium surface energy, hydrogen atom, helium atom, large-Z limit for noble gas energies, compressed

Ar<sub>2</sub>, and the large-Z limit of a 2-electron ion. Notable successes of SCAN, not previously achieved by PBE, include accurate description of both molecules and solids,<sup>303</sup> accurate critical pressures for structural phase transitions,<sup>304</sup> accurate transition metal surface energies and work functions, particularly if long-range dispersion corrections are included,<sup>305</sup> water dynamics,<sup>306</sup> and structure stability of main group compounds approaching chemical accuracy.<sup>307,308</sup> However, SCAN accuracy for cohesive energies of strongly bound solids is not superior to PBE's.<sup>309</sup>

SCAN shows only limited improvement over other LDA, GGA, and meta-GGA functionals for stabilities of transition metal compounds<sup>308,310</sup>; it underestimates reaction barriers and band gaps, and overestimates hydrogen bond strengths.<sup>302,303</sup> These drawbacks are associated with deficiencies of the (semi)local functional form (6.35), which is a core of all those methods, necessitating a different approach to the functional development. The underlying cause is termed the "self-interaction error" (SIE), and the hybrid functionals, introduced in the next chapter, partially resolve it.

## 6.5.4 Hybrid Functionals

## 6.5.4.1 Self-interaction Error (SIE)

There are two kinds of SIE: one-electron and many-electron SIE.<sup>311</sup> To illustrate the former, it is instructive to consider an H atom containing 1 electron. Physically, there are only two terms present in the total energy expression – kinetic energy and Coulomb energy of electron-nucleus interaction. However, a standard DFT expression (6.32) or (6.33) will always contain the unphysical electron-electron self-interaction energy  $U[\rho]$ , which should be canceled exactly by  $E_x[\rho]$  to obtain a physically realistic result. Because of the sum rules (6.38), such cancellation is nearly

perfect for GGA and meta-GGA, if the H orbital contains an integer number of electrons (1). However, if it contains a fractional number n (e.g., 0.5) on average due to electron transfer/delocalization to other parts of the system, this is no longer the case. For,  $U[\rho]$  formally scales as  $n^2$ , whereas, for example, LDA scales as  $n^{4/3}$ , so that  $-E_{xc}[\rho] = 0.5^{4/3} \approx 0.40 > 0.25 = 0.5^2 = U[\rho]$ , i.e.,  $E_{xc}[\rho]$  overcorrects  $U[\rho]$ , lowering the energy too much (compared with n = 1).

The many-electron SIE effect is a significantly complex more phenomenon, which amounts to similar energy lowering for fractional occupancies of a highest occupied molecular orbital (HOMO). The effect manifests itself in energy deviations from the exact



Figure 6.1. Difference energy of the carbon atom against the total electron number. Adopted from.<sup>2</sup>

straight lines, connecting neighboring total electron numbers N-1 and N, N+1 and N (Figure 6.1).

Since the total number of electrons in a system is an integer number, the fractional orbital occupancy is indicative of electron delocalization, favored by SIE. In transition states with natural delocalization due to nearly degenerate orbitals, the SIE lowers their energy, leading to reaction barrier underestimation. Transition metal compounds contain electrons localized on d-orbitals; their erroneous delocalization

may lead to wrong predictions of, e.g., a metallic state instead of a semiconducting one (as in NiO and other 3d compounds). Finally, deviations from the straight line (Figure 6.1) lead to slope deviations near N, which define the band gap.<sup>2</sup> Summing up, the SIE is accountable for all remaining deficiencies of semilocal functionals, described at the end of the previous subsection.

The intuitive solution to the 1-electron SIE was proposed by John Perdew and Alex Zunger as early as in 1981,<sup>312</sup> and was simply named the "self-interaction correction" (SIC):

$$E_{xc}^{SIC}[\rho] = E_{xc}^{sl}[\rho] - \sum_{i} (U[\rho_i] + E_{xc}^{sl}[\rho_i])$$
(6.60)

Here  $E_{xc}^{sl}$  is the approximate semilocal density functional and  $\rho_i$  is the electron density due to a single orbital. The SIC effectively replaces approximate selfinteraction correction part of  $E_{xc}[\rho]$  with the exact one. While the method showed some promise for atoms and improved reaction barriers, it overestimated the magnitude of the atomic exchange and total energy and led to poor thermochemistry and too short bond length predictions, which was attributed to upsetting the error cancellation balance between exchange and correlation<sup>313</sup> and poor description of noded densities by  $E_{xc}^{sl}$ .<sup>314</sup> In Chapter 6, we introduce the method, which, while resembles SIC by Perdew and Zunger, is free of such drawbacks. We achieve this by identifying and correcting the atomic self-interaction energy, transferable across bonded structures, as well as by taking advantage of the pseudopotential formalism, which smoothens radial nodes, and by accounting for the static correlation effects.

Many-electron SIE correction provides a better alternative to the original SIC. After inspection of the inset of Figure 6.1 one may realize that LDA (and GGA) deviations are downward (green line), whereas HF ones are upward (gray line). Therefore, one may hope that a smart combination of semilocal methods and HF will lead to a straight line, effectively eliminating SIE and its implications. This is the idea behind (global) hybrid functionals, first introduced by Becke in 1993.<sup>315</sup>

# 6.5.4.2 Global Hybrids

The notion of hybrid functionals follows naturally from PT. We stated previously that a combination of HF and the 4<sup>th</sup>-order Møller-Plesset PT (MP4) yields accurate atomization energies, especially for saturated compounds (2.6 kcal/mol mean absolute error).<sup>258</sup> Therefore, one may anticipate that by developing PT-like expressions within DFT, one can pave the way to more accurate approximations beyond meta-GGA.

In MP4 development, the electron-electron interaction term in the Hamiltonian is multiplied by a coupling constant  $\lambda$ , followed by the Taylor series expansion of energy eigenfunctions and eigenvalues in  $\lambda$ . A similar procedure can be implemented within the Kohn-Sham (KS) formalism, leading to the so-called adiabatic connection theorem.<sup>316</sup> The KS Hamiltonian corresponds to non-interacting electrons, moving in an average Kohn-Sham potential  $v_{KS}$ :

$$\widehat{H}_{KS} = \widehat{T} + v_{KS} \tag{6.61}$$

Since the Kohn-Sham theory is formally exact, its ground state energy and electron density are identical to that produced by the Schrodinger equation, with a Hamiltonian (6.62):

$$\widehat{H} = \widehat{T} + v_{ext} + V_{ee} \tag{6.62}$$

Here  $v_{ext}$  is an external potential due to nuclei, and  $V_{ee}$  is the Coulombic electron-electron interaction term. Equation (6.63) generalizes (6.61) and (6.62):

$$\widehat{H_{\lambda}} = \widehat{T} + v_{\lambda} + \lambda V_{ee} \tag{6.63}$$

For  $\lambda = 1$ ,  $v_{\lambda} = v_{ext}$ , whereas for  $\lambda = 0$ ,  $v_{\lambda} = v_{KS}$ .  $H_{\lambda}$  gives rise to the  $\Psi_{\lambda}$  many-electron wave function. All 3 equations yield identical electron densities. The  $\lambda$ -dependent ground state energy is:

$$E = E_{\lambda=1} = E_{\lambda=0} + \int dE = E_{\lambda=0} + \int_{\lambda=0}^{1} \frac{dE}{d\lambda} d\lambda$$
(6.64)

From the easily provable Hellman-Feynman theorem,<sup>255</sup> one has

$$\frac{dE}{d\lambda} = \left\langle \Psi_{\lambda} \left| \frac{d\widehat{H_{\lambda}}}{d\lambda} \right| \Psi_{\lambda} \right\rangle = \left\langle \Psi_{\lambda} \right| V_{ee} \left| \Psi_{\lambda} \right\rangle + \int \rho(\mathbf{r}) \frac{v_{\lambda}(\mathbf{r})}{d\lambda} d\mathbf{r}$$
(6.65)

We also have

$$E_{\lambda=0} = T_s + \int \rho(\mathbf{r}) v_{\lambda=0}(\mathbf{r}) d\mathbf{r}$$
(6.66)

After combining (6.64), (6.65), and (6.66), we get

$$E = T_s + \int \rho(\mathbf{r}) v_{ext}(\mathbf{r}) d\mathbf{r} + \int_{\lambda=0}^{1} V_{ee,\lambda} d\lambda$$
(6.67)

Finally, after removing the long-range,  $\lambda$ -independent Hartree term U, we get the following expression for the exchange-correlation functional:<sup>317</sup>

$$E_{xc} = \int_{\lambda=0}^{1} E_{xc,\lambda} d\lambda \tag{6.68}$$

Here  $E_{xc,\lambda}$  is a potential energy part of the exchange-correlation functional. According to the Gorling-Levy perturbation theory,<sup>318</sup> which is analogous to the Møller-Plesset theory, the exchange-correlation energy can be expanded in a series  $(\lambda = 1)$ :

$$E_{xc} = E_x + \sum_{n=2}^{\infty} E_c^{GLn} \lambda^n$$
(6.69)

Consequently,  $E_{xc,\lambda}$  can be expressed in a polynomial form of the  $(n-1)^{th}$  order:<sup>319</sup>

$$E_{xc,\lambda} = E_x + \sum_{n=2}^{\infty} E_c^{GLn} n \lambda^{n-1}$$
(6.70)

Coefficients  $E_c^{GLn}$ scale unfavorably with the system size ( $\sim N^5$ and above) and are very expensive to calculate. In addition, the series often converges slowly or does not converge at all.<sup>320</sup> At the same time, typical  $E_{xc,\lambda}$ curves, both calculated exactly<sup>321</sup> and approximated at the DFT level,<sup>3</sup> are featureless and represent simple, decreasing  $(E'_{xc,\lambda} < 0)$ monotonically functions with  $E''_{xc,\lambda} > 0$  (Figure 6.2). This immediately suggests a possibility of



Figure 6.2. The dependence of the  $E_{xc,\lambda}$  contribution to the negative of the N<sub>2</sub> dissociation energy upon  $\lambda$ . Adopted from.<sup>3</sup>

restoring the curve and thus approximating  $E_{xc}$  using much less information than

provided by the PT, making computations much less expensive. Seidl, Perdew, and Kurth<sup>319</sup> introduced the  $E_{xc,\lambda}$  functional expression that correctly describes the  $\lambda = 0$  (pure Hartree-Fock exchange) and  $\lambda \to \infty$  limits, while reproducing the 2<sup>nd</sup>-order PT coefficient  $E_c^{GL2}$ , and found that its non-self-consistent application to pre-optimized Kohn-Sham orbitals yields molecular atomization energies with MAE of 4.3 kcal/mol. The development of the MCY functional by Weitao Yang and co-workers was done in a similar fashion via proposing a 3-parameter  $E_{xc,\lambda}$  functional form.<sup>322</sup>

An even more pragmatic, computationally less expensive approach makes use of the semilocal functional and does not require expensive PT calculations. Evidently,  $E_{xc,\lambda=0} = E_x$ , where the latter is calculated exactly within the HF theory. Since a semilocal DFT functional relies heavily on error cancellation between nonlocal exchange and nonlocal correlation, and  $E_{xc,\lambda=0}$  does not contain any correlation, it is clear that the semilocal exchange would be a poor approximation to  $E_{xc,\lambda=0}$ , and this limit should be described by the exact exchange from HF. When moving from  $\lambda = 0$ toward  $\lambda = 1$ , more and more PT terms in (6.70) gradually become important, and the complexity of equations increases, with  $\lambda = 1$  corresponding to the most complex form, when the series formally diverges. However, in the subsection 6.3 we argued that statistical (semilocal) approximations are especially suitable for complex functional forms. Therefore,  $E_{xc,\lambda=1} = E_{xc,\lambda=1}^{sl}$ , with the latter obtained from, e.g., PBE functional. For intermediate  $\lambda$  values, Perdew, Ernzerhof, and Burke<sup>3</sup> proposed the following expression for  $E_{xc,\lambda}$  that interpolates between  $\lambda = 0$  and  $\lambda = 1$  limits, has an (n-1)th order polynomial form, negative first, and positive second derivatives, and does not require explicit calculations of  $E_c^{GLn}$  elements:

$$E_{xc,\lambda} = E_{xc,\lambda}^{sl} + (E_x - E_x^{sl})(1 - \lambda)^{n-1}$$
(6.71)

Substitution of (6.71) into (6.68) yields a remarkably simple expression:

$$E_{xc}^{hyb} = E_{xc}^{sl} + \frac{1}{n}(E_x - E_x^{sl}) = \left(1 - \frac{1}{n}\right)E_x^{sl} + \frac{1}{n}E_x + E_c^{sl}$$
(6.72)

(6.72) indicates that, to obtain an accurate approximation to the correct adiabatic connection curve and thus to the exact functional, it is only needed to take a weighted sum of the exact and approximate exchange energies, plus the approximate exchange! This is the essence of the (global) hybrid functional.

Since MP4 predicts atomization energies of a diverse set of molecules with a low MAE, it was argued<sup>3</sup> that the most optimal value of *n* is 4, corresponding to the 25% exact+75% semilocal (PBE) exchange combination (PBE0 functional<sup>323</sup>). The n = 4 choice also matches  $E_{xc,\lambda}^{DFA}$ 's slope and second derivative.

As the range of exchange interaction decays exponentially as a function of a band gap, the convergence of the exchange term  $E_x$  of a hybrid functional in metals and small-band-gap semiconductors becomes particularly slow,<sup>324</sup> making the method extremely expensive. The solution was to treat short-range and long-range parts of the PBEO exchange functional separately via splitting the Coulomb operator as follows: <sup>324</sup>

$$\frac{1}{r} = \frac{erfc(\omega r)}{r} + \frac{erf(\omega r)}{r}$$
(6.73)

Short-range exchange is treated at both the PBE and exact levels, whereas the long-range exchange is treated semilocally. This class of functionals is referred to as *range-separated hybrid functionals*. The adjustable parameter  $\omega$  was set to 0.4 in

HSE03<sup>324</sup> and was revised to 0.11 in HSE06 functionals.<sup>325</sup> The HSE performance is similar to PBE0 at much lower computational cost.

PBE0 shows improvement over PBE in terms of molecular geometries and atomization energies (8.6 vs. 3.7 kcal/mol MAE),<sup>326</sup> as well as hydrogen bonding in water,<sup>327</sup> and predicts molecular UV-vis spectra,<sup>328</sup> reaction barriers, NMR shielding,<sup>329</sup> and excitation energies<sup>330</sup> in better agreement with experiment.<sup>323</sup> Similar improved performance is peculiar to HSE. Both PBE0 and HSE predict much more reasonable band gaps,<sup>331</sup> which translates to correct material assignment regarding electron conductivity class of materials (semiconductor or metal) and improved site preference in CO adsorption on metals.<sup>332</sup> Magnetic properties and band structure of semiconductors are also described well.

Despite promising performance for molecules and semiconductors, results are less enlightening for metals and large-gap insulators.<sup>333</sup> The HSE underestimates considerably cohesive energies in transition metals; magnetic moments and overestimates phase transition pressures.<sup>299</sup> Binding energies of molecular metal hydrides are substantially overestimated by hybrids, similar to semilocal methods.<sup>294</sup> Bandwidth overestimation translates to CO overbinding, even to a larger extent than already present in PBE.<sup>332</sup> In insulators, band gaps and cohesive energies are better described in comparison with PBE, but are still underestimated. <sup>333</sup> Metal surface energies show no improvement over PBE.<sup>334</sup> Description of rare-earth oxides is also problematic – band gaps are overestimated, whereas reduction energies are underestimated.<sup>335</sup> Particularly poor performance of global hybrid functionals for transition metals renders them inapplicable for systems involving metal-adsorbate and metal-oxide interfaces.

Inconsistent performance of global hybrid functionals is associated with the following drawbacks:

- The n value in (6.72) is system-dependent. In the n<sup>th</sup> order PT, m<sup>th</sup> order terms (m ≤ n) are proportional to <sup>1</sup>/<sub>(ε<sub>ν</sub>-ε<sub>0</sub>)<sup>m-1</sup></sub>, as in (6.27), where ε<sub>ν</sub> and ε<sub>0</sub> are virtual and occupied orbital energies. As a first approximation, (ε<sub>ν</sub> ε<sub>0</sub>) can be associated with the band gap of the material. Consequently, for large-gap materials PT converges rapidly, and small n values should be used (e.g., 2). For metals with no band gap, PT diverges, equivalent to n → ∞, or 0% admixed exact exchange, consistent with the fact that metals exhibit slowly varying electron densities and are thus described well by semilocal functionals. The excellent performance for semiconductors indicates that n = 4 is probably optimal for this class of materials.
- 2) Hybrids overestimate static correlation. The static correlation error (SCE) arises in systems containing degenerate states, e.g., a hydrogen atom with spin-up/spin-down states of equal energy. In an exact theory, any linear combination of states (formally corresponding to fractional spins) should have the same energy. However, in semilocal DFT methods, their energy is overestimated (Figure 6.3)<sup>1</sup> non-spin-polarized atoms incorrectly have greater energy than spin-polarized ones. According to Figure 6.3, SCE in HF is worse than in semilocal methods, and thus hybrids that involve their linear combination, also exhibit greater SCE. This leads to poor magnetic property predictions in magnetic metals, poor cohesive energies,<sup>333</sup> and

erroneous prediction of paramagnetic ground states, rather than correct diamagnetic ones, for conducting oxides, such as RuO<sub>2</sub> and IrO<sub>2</sub>.<sup>336</sup>



Figure 6.3. Left: Potential energy curve of the  $H_2$  molecule, as described by HF, LDA, and a hybrid functional (B3LYP). Right: The H atom energy as a function of spin polarization. Adopted from Ref.<sup>1</sup>.

- 3) Hybrids are considerably more expensive than semi-local functionals. PBE0 is up to a factor of 3 more expensive than PBE for small molecules<sup>326</sup> and silicon;<sup>337</sup> HSE is as much as 3 orders of magnitude more expensive for MoO<sub>2</sub>.<sup>338</sup> This makes them essentially inapplicable to low symmetry systems, such as surfaces.
- Hybrids often involve an empirical parameter, fitted to bonded systems. Therefore, their transferability to systems not in the training set is uncertain.

In Chapter 6, we introduce a hybrid-type functional, which eliminates most of these drawbacks.

# 6.5.4.3 Hybrids with 100% Exact Exchange and Local Hybrids

To eliminate the global hybrid functional drawbacks, two approaches have been proposed.

One direction is to employ 100% exchange, essentially eliminating the systemdependent parameter n. In the long-range-corrected hybrid functional LC- $\omega$ PBE,<sup>339</sup> the Coulomb operator is split into short-range and long-range terms in vein of (6.73); however, unlike in HSE, the former is treated fully semilocally, whereas the latter is replaced with 100% exchange. The resulting functional is remarkably accurate for equilibrium thermochemistry, reaction barriers, as well as long-range charge transfer, with promising results for dissociation of symmetric radical cations.<sup>339</sup> Its success prompted development of a whole class of semiempirical long-range-corrected functionals, particularly by Head-Gordon and co-workers ( $\omega$ B97X-D).<sup>340</sup> However, LC-wPBE shows no considerable improvement in hydrogen affinities and selfinteraction error removal, as well as only moderate improvement for hydrogen-bonded complexes. It is clear, however, that its application to solids, especially conducting solids, would be computationally very expensive due to slow convergence of the longrange exact exchange. The most recent Becke functionals B05<sup>341</sup> and B13<sup>342</sup> also employ 100% exchange; a sophisticated procedure was developed to determine the degree of correlation nonlocality to make the correlation part compatible with the nonlocal exact exchange. These functionals were designed to address all known problems associated with semilocal DFT approximations, at the expense of increased computational cost even in comparison with global hybrids, abandonment of the uniform electron-gas limit (probably inconsequential for molecules), and "fine-tuning" of 5 (or 13) parameters. The use of exact exchange makes them inapplicable to catalysis problems.

The second direction aims to eliminate system dependence of the parameter n in the hybrid functional (6.72) by making n coordinate-dependent (6.74). The motivation is the following: upon moving toward high density or rapidly varying electron density regions, correlation and thus error cancellation vanish, requiring 100% exact exchange admixture. Since all finite and infinite systems of atoms contain a variety of electron density regions – slowly- (bond mid-points) and rapidly-varying (atomic tails), low and high (near cores) densities, it was argued that the exact exchange fraction should also vary in space, differentiating between "normal" and "abnormal" density regions.

$$E_{xc}^{l-hyb} = E_{xc}^{DFA} + \frac{1}{n(\mathbf{r})} (E_x - E_x^{DFA})$$
(6.74)

The key challenge in development of local hybrids is the functional form for  $n(\mathbf{r})$ . Unlike LDA and GGA, for which there are fundamental constraints and scaling relationships that inform analytical expressions and parameter values, essentially no additional constraints (except 1) are available at the hybrid level. As a result, a plethora of local hybrids have been introduced, varying in density abnormality measures, analytical expressions, and a number of empirical parameters. Jaramillo et al.<sup>343</sup> has chosen  $\frac{1}{n(\mathbf{r})} = \frac{\tau_W}{\tau}$  (compare to (6.54)), which correctly gives 1 for 1-electron and 0 for flat regions. The method improved most problematic cases (H<sub>2</sub><sup>+</sup>, barriers) at the expense of correct thermochemistry. A more systematic approach was taken by Perdew et al. (PSTS functional),<sup>344</sup> who introduced 2 density-dependent
variables,  $\frac{\epsilon_c^{GLSTPSS}}{\epsilon_x^{LSD}}$  and  $\frac{\epsilon_x^{ex}}{\epsilon_x^{TPSS}}$  that distinguished normal/abnormal regions and integer/fractional occupancies of orbitals, respectively. Those two ingredients were incorporated into  $\frac{1}{n(\mathbf{r})}$  in a highly complicated manner. After 5 parameters were fitted to thermochemistry and barriers, PSTS described the former with similar accuracy to the global hybrid TPSSh, and showed considerable improvement for barriers. However, PSTS (as well as all other developed local hybrids) still show considerable many-electron self-interaction and spin-polarization errors.<sup>345</sup> Similar to global hybrids, local hybrids require calculation of full exact exchange, which makes them prohibitively expensive for catalysis applications.

### 6.6 Summary and Outlook

There is multitude of ways to solve the Schrodinger equation approximately and yield chemically relevant information, and DFT is undoubtedly the most pragmatic approach. Despite a plethora of DFT functionals, reviewed here, there is no single method that is nearly exact for all property predictions. Hybrid functionals are able to correct DFT errors beyond traditional semilocal methods, but are expensive, empirical, and non-optimal. Is there a path forward to achieve higher accuracy at minimal extra cost and make computational catalysis more predictive? There is indeed, and one such method is introduced in Chapter 7.

### Chapter 7

# DFT+JJ: NON-EMPIRICAL DENSITY FUNCTIONAL FOR CHEMISTRY, MATERIALS SCIENCE, AND CATALYSIS APPLICATIONS

#### 7.1 Abstract

Accurate description of chemical bond energetics is a pivotal part of computational chemistry and catalysis. It ultimately determines the level of success and predictive ability of quantum mechanical models. Density functional theory (DFT) together with the generalized gradient approximation (GGA) is inarguably the method of choice for modeling surface phenomena in heterogeneous catalysis due to its optimal accuracy-to-cost ratio. Despite the success of GGA functionals (PBE, RPBE, PW91) in describing chemistry on metal surfaces, the GGA-inherent self-interaction error poses challenges for accurate treatment of processes on semiconductor surfaces, such as oxides.

Herein, we reveal the inadequacy of the PBE functional for describing experimental trends on metal oxide surfaces (e.g., RuO<sub>2</sub>, TiO<sub>2</sub>) for the vacancycatalyzed furfuryl alcohol hydrodeoxygenation, using first principles microkinetic modeling. We attribute the error to nonsystematic deviations of metal-oxygen bond energetics from experimental values. By utilizing adiabatic connection and the n<sup>th</sup> order perturbation theory, we arrive at an orbital-occupancy-dependent correction to the PBE functional that holds promise in mitigating the DFT accuracy problem. Corrections are formulated in the spirit of the DFT+U method. The new PBE-based *non-empirical* functional demonstrates clear improvement over pure PBE in describing dissociation energetics of molecules, cohesive energies of solids, lattice constants, and atomic and molecular ionization energies, at minimal extra computational cost.

# 7.2 Motivation

In Section 6.5.4.1, we described the self-interaction error (SIE) of semilocal density functionals (LDA, GGA, meta-GGA) and its detrimental effect on property predictions of transition metal compounds. SIE also manifests itself in catalysis applications, preventing quantitative prediction of reaction rates on metal oxide catalysts.

In Figure 7.1, we compare furfuryl alcohol hydrodeoxygenation rates, predicted from *ab initio*-parameterized microkinetic models (MKM), with experimental values, which we already reported in Figure 4.2. Evidently, the reactivity trend cannot be reproduced. All those early MKMs did not incorporate more recent knowledge about 2 vacancy formation mechanisms (Figure 4.5), a proper referencing scheme (Section C.4.3), and DFT model geometry constraints (Table C.5), which could have been at least partially responsible for such discrepancies. However, the wrong reactivity order of RuO<sub>2</sub> and IrO<sub>2</sub> is particularly troubling, since both materials have a rutile crystal structure, are conductors, and exhibit the same vacancy formation mechanism (Figure 4.5). The RuO<sub>2</sub> MKM predicted the reaction mechanism and kinetics in close agreement with the experiment,<sup>8</sup> and thus the same level of agreement would be expected for IrO<sub>2</sub>.

To explain this difference, we tested two hypotheses: (1) different facets are

responsible for the catalytic activity, and (2)IrO<sub>2</sub> exhibits a different, Lewis acid site-mediated C-O scission mechanism. In Table 7.1 we report HDO reactivity descriptor values (OH binding energies; see Section C.1) on various facets and surface binding



Figure 7.1. Comparison of predicted and experimental furfuryl alcohol hydrodeoxygenation rates. The PBE semilocal functional was used in calculations. The reactivity of (110) facets is assumed to be representative of the entire catalyst surface.

sites. The  $IrO_2(110)$  vacancy binds OH stronger than the RuO<sub>2</sub>(110), consistent with lower predicted rates on the former (Figure 7.1). OH binding is comparable or weaker on other  $IrO_2$  facets as well (Table 7.1) – the first hypothesis is not confirmed. The second hypothesis is also falsified by the evidence – although  $IrO_2(110)$  Lewis acidic sites bind OH stronger than those of RuO<sub>2</sub>(110) (inactive for this reaction<sup>4</sup>), which should translate to greater catalytic rates, they also exhibit high affinity to H, such that in a reducing environment, all  $IrO_2$  Lewis acid sites are completely covered with hydrogen (Figure 4.4).

	OH binding energies, eV			
Facets	RuO <sub>2</sub>		IrO <sub>2</sub>	
	Vacancy	Lewis acid site	Vacancy	Lewis acid site
(110)	-0.89	-0.26	-1.04	-0.63
(101)	-1.62	-0.70	-0.88	-0.97
(100)	-1.00	-1.62	-1.00	-1.37

Table 7.1. OH electronic binding energies relative to H<sub>2</sub> and H<sub>2</sub>O.

i.

Further analysis revealed that the most likely source of discrepancies between predicted and experimental reaction rates lies in the density functional. In Table 7.2, we report errors in DFT predictions of reaction enthalpies relative to experimental data. The two reactions are related to formation and cohesive energies of oxides, respectively, and reflect the accuracy of M-O bond strength predictions in oxide materials:

- 1)  $M(bulk) + 2H_2O(gas) = MO_2(bulk) + 2H_2(gas)$
- 2)  $M(gas) + 2H_2O(gas) = MO_2(bulk) + 2H_2(gas)$

Here M is Ti, Sn, Ru, or Ir. We accounted for translational, rotational, and vibrational degrees of freedom in  $H_2$  and  $H_2O$  calculations; for bulk materials we assumed an Einstein crystal model with M and O vibrational energy contributions taken to be identical to those in  $RuO_2$  (Section B.1).

Table 7.2. Differences between predicted and experimental reaction enthalpies at 298K. The PBE density functional is used.

Reaction enthalpy errors, eV	TiO <sub>2</sub>	SnO <sub>2</sub>	RuO <sub>2</sub>	IrO <sub>2</sub>
Reaction 1	+0.35	+0.72	-0.22	-0.21
Reaction 2	-0.21	+0.73	-0.24	-0.53

The data in Table 7.2 indicate that (1) there are substantial errors in M-O bond strength predictions in metal oxides when the PBE functional is employed and (2) there is no systematic trend in errors. The latter observation is profoundly important. Semilocal functional errors are well known; however, they have no consequence on reactivity trend predictions on transition metal catalysts,<sup>346</sup> because the errors are systematic in nature (e.g., the PBE systematically overbinds adsorbates on metals). Evidently, this is not the case with metal oxides. Perhaps this can explain the scarcity of reported comparisons between explicitly computed and experimentally measured reaction rates over metal oxide catalysts. Semilocal functionals (PBE) do not describe energetics of metal oxides well.

We tested other classes of functionals (meta-GGA, hybrids), but were unable to identify a method that consistently improves predictions of metal oxide energetics. For SnO<sub>2</sub>, which exhibits the most substantial errors, meta-GGA (TPSS) and hybrid (HSE) functionals yield no significant improvement in reaction 2 enthalpy predictions. The errors are +0.53 and +1.28 eV, respectively. The widely used semiempirical M06-L meta-GGA did not converge. Clearly, there is a need for functionals that would describe oxide materials accurately. We introduce one such method in this Chapter.

### 7.3 Method Development

#### 7.3.1 DFT+U

Curiously, we identified one method that nearly eliminates the reaction 2 error in  $SnO_2 - DFT+U$ . In the simplest implementation of the DFT+U method due to Dudarev et al.,<sup>212</sup> the semilocal functional (PBE) is complemented with atom-centered corrections that depend on occupancies of the localized *d* and/or *f* atomic orbitals:

$$E_{xc+U} = E_{xc}^{sl} + \frac{U}{2} \sum_{a=1}^{N} \sum_{m=1}^{2L+1} \sum_{\sigma} (o_{am\sigma} - o_{am\sigma}^2)$$
(7.1)

Summations are over atoms *a*, magnetic quantum numbers *m* corresponding to *d* or *f* atom subshells (azimuthal quantum number L = 2 or 3, respectively), and up and down electron spins  $\sigma$ . The  $o_{am\sigma}$  is the orbital occupancy, which is a probability of finding an electron in a particular orbital. Occupancies can take values between 0 and 1. The parameter *U* represents a Coulomb energy cost to place two electrons on the same orbital. U is system-specific and is most frequently determined empirically; rigorous ways to determine it either from constrained DFT<sup>347</sup> or linear response theory<sup>348</sup> also exist. The method is only marginally more expensive than semilocal DFT and amounts to penalizing non-integer occupancies over integer ones, since the second term in (7.1) is positive, unless  $o_{am\sigma} = 0$  or 1. As fractional occupancies correspond to electron delocalization, DFT+U effectively corrects SIE, acting in a similar vein as hybrid functionals.

It is quite exciting that a single U parameter value (3.5 eV), calculated from the first principles,<sup>214</sup> nearly eliminates errors in both the cohesive energy and the lattice constant of SnO<sub>2</sub>. However, DFT+U performance is typically less thrilling for other systems. It yields unacceptable reaction 2 (cohesive energy) error for TiO<sub>2</sub> (+1.23 eV for U=3.5 eV). The lattice constant is also overestimated (a=4.64, 4.66, and 4.59 Å for PBE, PBE+U, and experiment, respectively). It is well-known that improvement of 3 different properties – band gap, structure, and formation energy differences - requires 3 different U values.<sup>349</sup> Moreover, the U value depends on material geometry<sup>350</sup> and oxidation state.<sup>349</sup> DFT+U cannot be applied to conducting materials, including RuO<sub>2</sub> and IrO<sub>2</sub> – even at low U values (~ 1-2 eV), they incorrectly turn into

antiferromagnetic metals and then to Mott insulators, contrary to experimental evidence.<sup>351</sup> Such variability renders DFT+U at best as a specific-purpose semiempirical method that does not provide a systematic improvement toward "exact"  $E_{\rm XC}$  in a way GGA's, meta-GGA's, and hybrids do.

# 7.3.2 DFT+JJ

In 1998 Zhang and Yang<sup>352</sup> derived a scaling relationship, whereby they showed that the exact density functional satisfies  $E_{XC}[o\rho_1] = o^2 E_{XC}[\rho_1]$ , where *o* is the orbital occupancy, and  $\rho_1$  is one-electron density. The authors showed that for semilocal functionals, it is violated due to SIC ( $E_{XC}[o\rho_1] < o^2 E_{XC}[\rho_1]$ ; compare to Section 6.5.4.1). To prove this inequality, the authors showed in the appendix that the deviation is proportional to  $-(o^{4/3} - o^2)$  at the LDA level of theory, with extra terms for GGA, and thus is always nonpositive. This expression is remarkably similar to that of DFT+U (7.1), except for the power of 4/3 instead of 1. We hypothesized that (7.1) is not optimal, and the 4/3 exponent is better justified on DFT grounds. We replaced (7.1) with (7.2) in the VASP quantum chemical software, with the concomitant replacement of the one-electron potential expression (*vide infra*):

$$E_{xc} = E_{xc}^{sl} + \frac{J_1}{2} \sum_{a=1}^{N} \sum_{m=1}^{2L+1} \sum_{\sigma} o_{am\sigma}^{4/3} - \frac{J_2}{2} \sum_{a=1}^{N} \sum_{m=1}^{2L+1} \sum_{\sigma} o_{am\sigma}^2$$
(7.2)

We obtained promising results for SnO<sub>2</sub>, when  $J_1$  and  $J_2$  were treated as empirical parameters, but there was room for improvement for TiO<sub>2</sub>. To increase the accuracy, we decided to apply occupancy-dependent corrections not only to *d* orbitals, but also to *p* orbitals, using the following qualitative argument. If we consider PBE functional performance for elements of the group 14 of the Mendeleev Periodic Table, we find that it predicts cohesive energies of diamond, silicon, germanium, SiO<sub>2</sub>, and GeO<sub>2</sub> very accurately, which we attribute to the fact that the metal-oxygen bond (M-O) is of *sp-sp* type, involving *s* and *p* orbitals of metal and oxygen, and thus error cancellation occurs. Although tin belongs to the same group, SnO<sub>2</sub> differs from the above materials by semicore d-states of Sn, treated as valence electrons, so that the bonding is of *dsp-sp* type. As there are no d states available in O, no error cancellation occurs, so that PBE performs poorly for SnO<sub>2</sub>. (7.2) corrects inherent errors in *d*-orbitals, restoring the accuracy of the *sp-sp* bonding and eliminating energetic and structural errors. In TiO<sub>2</sub>, however, the chemical bonding is of *ds-sp* type; error cancellation occurs to a lesser extent due to different topology of p and d orbitals. Therefore, if the SnO<sub>2</sub> argument is correct, TiO<sub>2</sub> calculations can be improved, if both *d* orbitals of Ti and *p* orbitals of O are corrected.

We extended the modified DFT+U method to *p* orbitals and chose an O<sub>2</sub> molecule as a test system – it is known to be challenging for semilocal methods. We set the  $J_2$  parameter in (7.2) equal to  $F^2/5$ , where  $F^2$  is a Slater integral, a fraction of the exact exchange in the *p* subshell of a spherical, non-spin-polarized free O atom ( $J_2 = 4.46$  eV). In Figure 7.2 we



Figure 7.2.  $O_2 \rightarrow 2O$  dissociation electronic energy error relative to the experiment.

report the O<sub>2</sub> dissociation energy error as a function of  $J_1$ , treated as a parameter. The remarkable result is that the error is reduced to almost zero when  $J_1 = J_2$ ! According

to the Zhang-Yang scaling relationship,  $J_1$  can be interpreted as semilocal selfexchange of a singly occupied p orbital, and  $J_2$  is the corresponding exact exchange. Two quantities are related to two different electronic structure theories, and their equality cannot happen by chance and must have deep fundamental roots. Moreover, the equality leads to considerable method simplification – the Slater integrals defining  $J_2$  are fully transferable across all conceivable bonded structures a given atomic type participates in. Due to a different physical basis in comparison to DFT+U, we refer to the method as DFT+JJ, with J being a standard notation for the exchange integral.

Before DFT+JJ can be extended to other systems, it is crucially important to address the static correlation error (SCE). In Section 6.5.4.2, we mentioned it in the context of global hybrid functionals; since DFT+JJ is formally a hybrid, it inherits the same problem – the energy of non-spin-polarized atoms is considerably overestimated, due to a positive energy penalty for fractional occupancies in (7.2). It had no consequences for reactions involving only singlet or only triplet species (such as  $O_2$  dissociation in Figure 7.2), but led to considerable errors, when singlet and multiplet states are mixed in the same reaction, as in the majority of atomization reactions. We overcame this problem in two different ways: (1) by using non-spin-polarized atoms in atomization energy calculations as references, corrected by the SCE value, calculated at the PBE level of theory; and (2) by defining new occupancies, averaged over degenerate states:

$$\bar{o}_i = \frac{\sum_{m=1}^{2L+1} \sum_{\sigma} o_{m\sigma}}{2(2L+1)}$$
(7.3)



Figure 7.3. Comparison of (a) molecular atomization energy errors and (b) cohesive energy errors in metal oxides, calculated by PBE and PBE+JJ functionals, relative to experimental values.

In Figure 7.3, we compare atomization and cohesive energy errors of PBE and PBE+JJ functionals. The new JJ method substantially improves the accuracy of energy predictions over PBE and does not require any empirical parameters – J values are calculated directly from Slater integrals ( $J = (F^2 + F^4)/14$  for d orbitals). Unlike DFT+U and hybrids, DFT+JJ is applicable to conductors (RuO<sub>2</sub>, IrO<sub>2</sub>, Pt) – the occupancy averaging procedure prevents spin-symmetry breaking. Improvements in predictions of energetics come together with more accurate lattice constants (Table 7.3).

		Lattice constant errors, Å	
		а	с
SnO <sub>2</sub>	PBE	+0.08	+0.06
	PBE+U	0.00	-0.02
	PBE+JJ	+0.01	0
IrO <sub>2</sub>	PBE	+0.04	+0.04
	PBE+U	-	-
	PBE+JJ	+0.01	+0.01
TiO <sub>2</sub>	PBE	+0.04	+0.02
	PBE+U	+0.07	+0.06
	PBE+JJ	+0.04	+0.03
RuO <sub>2</sub>	PBE	+0.03	+0.02
	PBE+U	-	-
	PBE+JJ	+0.02	+0.01

Table 7.3. Comparison of PBE and PBE+JJ-calculated lattice constant errors of metal oxides relative to experimental values.

In Figure 7.4 we compare lattice constant predictions in bulk Pt using different methods. Again, nonempirical PBE+JJ yields nearly perfect agreement with the **RPBE**<sup>280</sup> experiment; and semiempirical BEEF,<sup>353</sup> widely adopted in heterogeneous catalysis significant studies, show deviations.

Figure 7.4 also contains an important fundamental result.



Figure 7.4. Energy of bulk Pt as a function of a lattice constant. PBE, PBE+JJ, BEEF, RPBE, and experimental values are shown for comparison.

Lattice constant overestimation by PBE has been previously attributed to the

functional bias to free atom energies - its gradient expansion coefficient for exchange is similar to that of semiclassical atoms.<sup>277</sup> PBEsol was designed to restore the correct gradient coefficient, improving LC predictions (Figure 7.4) at the expense of accurate energies, since atoms are described poorly. Consequently, it was concluded that the GGA functional form is too restrictive to accurately describe atoms and solids simultaneously. The success of DFT+JJ pinpoints a different cause of LC errors – SIE in the atomic limit. By correcting it, JJ allows accurate prediction of *both* energies and LCs, unlike PBEsol.

Finally, in Table 7.4 we access DFT+JJ performance for CO chemisorption energies on Pt(111). The non-empirical JJ correction reduces PBE overbinding considerably and exhibits accuracy on par with RPBE and semiempirical BEEF, specifically designed for metal surfaces.

	Adsorption energy, eV	Error, eV
Experiment	-1.29	-
PBE	-1.62	-0.33
RPBE	-1.41	-0.12
BEEF	-1.37	-0.08
PBE+JJ	-1.42	-0.13

Table 7.4. CO chemisorption energies on a top site of Pt(111), evaluated with different methods.

Despite very promising performance, the weak point of the DFT+JJ method is the averaging procedure, introduced in an *ad hoc* manner. There are different types of averaging, depending on degeneracies present in an atomic subsystem (spin up/down vs. magnetic quantum number degeneracy), and we found the choice of the averaging type to be material-specific. To avoid this, we developed a rigorous procedure for reducing SCE from quantum mechanical principles, described in Section 7.4.6. As a numerical test of the new procedure, in Table 7.5 we report energies of reactions involving hydrocarbons, for which the averaging procedure previously failed. Improvement over PBE is significant.

Table 7.5. Comparison of PBE and PBE+JJ with a revised SCE removal scheme for energy predictions of reactions of hydrocarbons.

	PBE error	PBE+JJ error
$2CH_4 = C_2H_4 + 2H_2$	0.11	-0.02
$2CH_4 = C_2H_2 + 3H_2$	0.25	0.06
$2CH_4+2C_2H_2=3C_2H_4$	-0.18	-0.18
$C+2H_2=CH_4$	-0.43	0.01
$2C+2H_2=C_2H_4$	-0.76	0.00
$2C+H_2=C_2H_2$	-0.62	0.08

This subsection highlighted the basics of the new DFT+JJ method, its development and encountered challenges. In the following subsection, we present its rigorous method formalism.

## 7.4 Formalism

### 7.4.1 Regional Hybrids

In quantum mechanics, the superposition principle (6.3) enables one to expand an arbitrary wave function in terms of the eigenfunctions of any physical quantity, to which there corresponds a Hermitian operator. Therefore, one-electron solutions of Kohn-Sham equations  $H_{KS}|\tilde{\varphi}\rangle = E_{KS}|\tilde{\varphi}\rangle$  can be expanded in terms of one-electron eigenfunctions of (7.4), which are referred to as the basis set functions. Here  $H_{KS} = T + V_{KS}$  and  $H_{basis} = T + V_{basis}$ , where T and V are kinetic and potential energy operators, respectively.

$$H_{basis}|\varphi\rangle = E_{basis}|\varphi\rangle \tag{7.4}$$

For a discrete  $|\varphi\rangle$  spectrum, the expansion is

$$\tilde{\varphi}_i(\mathbf{r}) = \sum_{\mu} C^i_{\mu} \varphi_{\mu}(\mathbf{r})$$
(7.5)

The electron density can be expanded in the basis set as

$$\rho(\mathbf{r}) = \sum_{i} f_{i} |\tilde{\varphi}_{i}(\mathbf{r})|^{2} = \sum_{i,\mu,\mu'} f_{i} C_{\mu}^{i} C_{\mu'}^{i} \varphi_{\mu}(\mathbf{r}) \varphi_{\mu'}(\mathbf{r})$$
(7.6)

Here  $f_i$  are the occupancies of Kohn-Sham orbitals. Basis set functions  $|\varphi\rangle$  can be assembled into groups  $\Gamma_1$ ,  $\Gamma_2$ , ..., such that  $\{\varphi_1, \varphi_2, ..., \varphi_n\} \in \Gamma_1, \{\varphi_{n+1}, \varphi_2, ..., \varphi_m\} \in$  $\Gamma_2$ , etc. Similarly, certain sums of the terms on the right-hand side of (7.6) can be associated with  $\Gamma_1, \Gamma_2, ...$ , based on the specific basis functions they contain, i.e.,

$$\rho_{\Gamma_{1}}(\mathbf{r}) = \sum_{i} \sum_{\mu=1,\mu'=1}^{\mu=n,\mu'=n} f_{i} C_{\mu}^{i} C_{\mu'}^{i} \varphi_{\mu}(\mathbf{r}) \varphi_{\mu'}(\mathbf{r})$$

$$\rho_{\Gamma_{2}}(\mathbf{r}) = \sum_{i} \sum_{\mu=n+1,\mu'=n+1}^{\mu=m,\mu'=m} f_{i} C_{\mu}^{i} C_{\mu'}^{i} \varphi_{\mu}(\mathbf{r}) \varphi_{\mu'}(\mathbf{r})$$

$$\vdots$$
(7.7)

Consequently, the electron density can be decomposed into several (potentially infinite) contributions, each defined on a subspace of the basis functions:

$$\rho(\mathbf{r}) = \sum_{i} \rho_{\Gamma_{i}}(\mathbf{r}) + \rho_{\text{int}}(\mathbf{r})$$
(7.8)

Here  $\rho_{int}(\mathbf{r})$  includes the terms in the summation of (7.6) that involve products of basis set functions belonging to different groups. It is trivial to show within the wave mechanics formalism<sup>256</sup> (a combination of Hartree-Fock theory and Configurational Interaction) that analogous decomposition into groups, defined by basis set subspaces, is possible for each term of the Kohn-Sham total energy expression (6.33). For the total energy,

$$E[\rho] = \sum_{i} E[\rho_{\Gamma_{i}}] + E_{\text{int}}$$
(7.9)

For the exchange-correlation functional,

$$E_{xc}[\rho] = \sum_{i} E_{xc}[\rho_{\Gamma_{i}}] + E_{xc,int}$$
(7.10)

From the properties of the Schrodinger equation it follows<sup>255</sup> that discrete eigenfunctions are localized in space; therefore, basis set groups  $\Gamma_i$  can be defined in such a way that each of them is associated with a particular volume of space. Since  $\rho_{\Gamma_i}$ 's are related to the total density of the system only by the projection operation onto the  $\Gamma_i$  subspace, they can be regarded as independent reference systems, and their properties can be exploited to arrive at better approximations for  $E_{xc}[\rho]$ . For example, if  $\rho_{\Gamma_i}$  resembles a homogeneous electron gas, then semilocal functionals should be used for  $E_{xc}[\rho_{\Gamma_i}]$ . If  $\rho_{\Gamma_j}$  is rapidly varying or one-electron-like, then  $E_{xc}[\rho_{\Gamma_j}]$  should employ 100% exact exchange. In parts of space where  $\Gamma_i$  and  $\Gamma_j$  exhibit substantial overlap, basis sets can provide a natural interpolation between the corresponding functionals  $E_{xc}[\rho_{\Gamma_i}]$  and  $E_{xc}[\rho_{\Gamma_j}]$ , akin to highly successful interpolative approaches within GGA (Section 6.5.2.1) and meta-GGA (equation (6.59)) methods.

Herein, we formally apply the exact scaling relationship  $(7.11)^{317}$  to  $E_{xc}[\rho_{\Gamma_i}]$ and  $E_{xc}[\rho]$ , which defines the adiabatic connection curve (Figure 6.2):

$$E_{xc,\lambda}[\rho] = \frac{d}{d\lambda} \left( \lambda^2 E_{xc} \left[ \frac{\rho(r/\lambda)}{\lambda^3} \right] \right)$$
(7.11)

The curve corresponding to  $E_{xc,int}$  can be obtained as  $E_{xc,\lambda}[\rho] - \sum E_{xc,\lambda}[\rho_{\Gamma_i}]$ . The resulting curves can be approximated by the polynomial (6.71), each with a unique highest polynomial order  $n_i$ , resulting in an ensemble of hybrid density functionals, which we refer to as the *regional hybrid*:

$$E_{xc}^{reg-hyb} = E_{xc}^{sl}[\rho] + \sum_{i} \frac{1}{n_{\Gamma_{i}}} \left( E_{x}[\gamma_{\Gamma_{i}}] - E_{x}^{sl}[\rho_{\Gamma_{i}}] \right) + \frac{1}{n_{int}} \left( E_{x}^{int}[\gamma] - E_{x}^{sl}[\rho_{int}] \right)$$
(7.12)

Here  $E_x$  is the exact exchange energy,  $E_x^{sl}$  is the semilocal approximation to exchange (PBE),  $\gamma = \sum_i f_i \tilde{\varphi}_i(\mathbf{r}) \tilde{\varphi}_i(\mathbf{r}')$  is the first-order density matrix, defined for electrons of the same spin (compare with (7.6)), and  $\gamma_{\Gamma_i}$  is its projection on  $\Gamma_i$ . The advantage of the regional hybrid (7.12) is that it can be made exact for paradigm densities (a homogeneous electron gas, one-electron density, atomic densities) by the proper choice of  $n_{\Gamma_i}$ . If  $\Gamma_i$  is a homogeneous gas and  $\rho = \rho_{\Gamma_i}$ , then  $n_{\Gamma_i} = \infty$  will reflect the fact that  $E_{xc}^{reg-hyb} = E_{xc}^{exact}[\rho] = E_{xc}^{sl}[\rho]$ ; if it is a one-electron density, then  $n_{\Gamma_i} = 1$ , since  $E_{xc}^{reg-hyb} = E_{xc}^{exact}[\rho] = E_x[\rho]$ .

Since the regional hybrid is a generalization of the global hybrid functional (6.72), it is instructive to compare it with another generalization – the local hybrid functional:

$$E_{xc}^{l-hyb} = E_{xc}^{DFA} + \frac{1}{n(\mathbf{r})} (E_x - E_x^{DFA})$$
(7.13)

Many semiempirical local hybrids have been proposed, but none is very successful. Herein we highlight one possible reason why. Equation (7.13) implies that each point in space **r** has an associated adiabatic connection curve  $E_{xc,\lambda}$ , fitted by the polynomial of the order  $n(\mathbf{r})$ . However, this is not possible, since the curve arises from the scaling relationship (7.11), involving an integral quantity  $E_{xc}\left[\frac{\rho(r/\lambda)}{\lambda^3}\right]$ , which evidently becomes zero at a dimensionless point **r**. In other words, the local hybrid functional is inconsistent with the adiabatic connection construction (6.71). On the other hand, our newly introduced *regional hybrid* does not have this drawback, since each  $n_{\Gamma_i}$  is associated with a *volume* of space, spanned by the basis subspace, for which  $E_{xc}\left[\frac{\rho(r/\lambda)}{\lambda^3}\right]$  is perfectly defined. We conclude that our regional hybrid (7.12) represents a better starting point to eliminate shortcomings of global hybrids (see Section 6.5.4.2) and make a true step toward the Holy Grail – the exact density functional.

#### 7.4.2 Atomic Regional Hybrid

In this subsection, we develop a type of the regional hybrid, named the atomic regional hybrid. First, we note that for all *finite* systems made of atoms, the oneelectron potential  $V_{KS} \rightarrow 0$  as  $\mathbf{r} \rightarrow \infty$ . Since the basis set Hamiltonian  $H_{basis} = T + V_{basis}$  is expected to be representative of real systems, we also have  $V_{basis} \rightarrow 0$  as  $\mathbf{r} \rightarrow \infty$ . In this case, however, the basis set spectrum  $|\varphi\rangle$  is discrete for eigenvalues  $E_{basis} < 0 \ (\varphi_{\mu})$  and continuous for  $E_{basis} > 0 \ (\varphi_{\nu})$ .<sup>255</sup> Therefore, (7.5) should be replaced by (7.14) for the real systems:

$$\tilde{\varphi}_{i}(\mathbf{r}) = \sum_{\mu} C_{\mu}^{i} \varphi_{\mu}(\mathbf{r}) + \int b_{\nu}^{i} \varphi_{\nu}(\mathbf{r}) d\nu$$
(7.14)

We assemble  $\varphi_{\mu}$  into only two groups – that of discrete and that of continuous basis set functions. (7.12) becomes

$$E_{xc}[\rho] = E_{xc}^{sl}[\rho] + \frac{1}{n_{\Gamma_{dis}}} \left[ E_x[\gamma_{\Gamma_{dis}}] - E_x^{sl}[\rho_{\Gamma_{dis}}] \right] + \frac{1}{n_{\Gamma_{cont}}} \left[ E_x[\gamma_{\Gamma_{cont}}] - E_x^{sl}[\rho_{\Gamma_{cont}}] \right] + \frac{1}{n_{int}} \left[ E_x^{int} - E_x^{sl,int} \right]$$

$$(7.15)$$

Here  $\rho_{\Gamma_{dis}}$  and  $\rho_{\Gamma_{cont}}$  are electron densities, spanned by discrete and continuous basis set functions, respectively. First-order density matrices  $\gamma_{\Gamma_{dis}}$  and  $\gamma_{\Gamma_{cont}}$  are defined in a similar way.

The most natural and universal  $V_{basis}$  choice, applicable to any chemically bound structure, is that of free atoms. In this case, the discrete basis set part is represented by atomic eigenfunctions, and  $\rho_{\Gamma_{dis}}$  is the electron density projection onto the atomic orbitals. The continuous basis set part in the  $V_{basis} \rightarrow 0$  asymptotic limit far away from the finite atomic system is then represented by plane waves.<sup>255</sup> Both discrete and continuous basis set parts are infinite. The requirement for an infinite set of discrete basis functions can be lifted, if one defines non-overlapping augmentation spheres surrounding each atom in a chemical system (Figure 7.5). The electronic density distribution within each sphere is weakly perturbed by chemical bonding, and thus it is similar to the distribution of a free atom, requiring a small basis set of atomic valence orbitals of either primitive or double-zeta quality (i.e., each atomic state is described by 2 functions) to describe it. Outside augmentation spheres, in atomic overlap regions of bonding orbitals, the



Figure 7.5. Electron density distribution in RuO<sub>2</sub>. Orange corresponds to more dense regions; blue - to less dense ones. Selected augmentation spheres are marked by dashed yellow circles. Radii of depicted circles are not representative of actual radii, used in VASP software.

effective potential  $V_{KS}$  is approximately constant, making plane waves, which are the exact Schrodinger equation solutions for a constant (nonpositive) potential, a natural basis set choice. A combination of a localized atomic basis set + delocalized plane waves has formed a basis of several electronic structure methods, such as the augmented plane wave method<sup>354</sup> or the projector-augmented wave (PAW) method.<sup>47</sup> We will proceed from (7.15) within the PAW formalism, as implemented in the VASP code.<sup>48</sup> For an atom A, we associate  $\rho_{\Gamma_{dis,A}}$  and  $\gamma_{\Gamma_{dis,A}}$  with the projection region  $\Omega_A$ , defined below, which is identical to the augmentation sphere region for the majority of the elements and is spanned by the standard PAW atomic basis set  $\Gamma_{dis,A}$ .  $\rho_{\Gamma_{cont}}$  and  $\gamma_{\Gamma_{cont}}$  are associated with the interatomic region, spanned by the plane waves form a

discrete, not a continuous basis; however, the separation between their energy levels is small.

In the PAW formalism, there is no coupling between atomic orbitals and plane waves, so that (7.15) is simplified as

$$E_{xc}[\rho] = E_{xc}^{sl}[\rho] + \sum_{A} \frac{1}{n_{\Gamma_{dis,A}}} \Big[ E_x \big[ \gamma_{\Gamma_{dis,A}} \big] - E_x^{sl} \big[ \rho_{\Gamma_{dis,A}} \big] \Big] + \frac{1}{n_{\Gamma_{cont}}} \Big[ E_x \big[ \gamma_{\Gamma_{cont}} \big] - E_x^{sl} \big[ \rho_{\Gamma_{cont}} \big] \Big]$$
(7.16)

Since the electron density varies slowly in the interatomic region (Figure 7.5) and thus resembles a nearly homogeneous electron gas, we hypothesize that the semilocal exchange is a good approximation to the exact one, i.e.,  $E_x[\gamma_{\Gamma_{cont}}] = E_x^{sl}[\rho_{\Gamma_{cont}}]$ , and thus the last term in (7.16) is zero. However,  $E_x[\gamma_{\Gamma_{dis,A}}] \neq E_x^{sl}[\rho_{\Gamma_{dis,A}}]$ , since the density is inhomogeneous and high in the atomic region; exchange dominates over correlation at those conditions,<sup>14,344</sup> and thus the error cancellation between exchange and correlation (Section 6.5.1) should be not efficient. Moreover, the nodal structure of atomic orbitals is challenging for semilocal methods<sup>355</sup> (as well as for DFT-SIC<sup>314</sup>).

The simplified regional hybrid functional (referred to as the *atomic regional hybrid*) takes the following form:

$$E_{xc}[\rho] = E_{xc}^{sl}[\rho] + \sum_{A} \frac{1}{n_{\Gamma_{dis,A}}} \Big[ E_x \big[ \gamma_{\Gamma_{dis,A}} \big] - E_x^{sl} \big[ \rho_{\Gamma_{dis,A}} \big] \Big]$$
(7.17)

The functional form (7.17) corrects the atomic density region, not properly described by semilocal methods. It is important to note that, after the neglect of  $E_x^{sl}[\rho_{\Gamma_{cont}}]$  corrections, the error remains in the regions of overlapping lone electron

pairs (as in He<sub>2</sub> or Ar<sub>2</sub>), described poorly by semilocal methods. The error has no relevance to the systems with predominant covalent and metallic bonding and can be improved by meta-GGA<sup>302</sup> or by certain GGA's (PBE) that mimic van der Waals interaction.<sup>356</sup>

The methods employing atomic corrections have been remarkably successful in the past – least-square-fit, empirical atomic energy corrections reduced MAE of molecular atomization energies from 217.7 to 4.4 kcal/mol at the LDA (!) level of theory (SVWN5), and from 32.2 to 2.2 kcal/mol using the PBE functional.<sup>357</sup>. Fitted elemental-phase reference energies reduced formation energy errors of 252 binary solids from 0.25 to 0.054 eV/atom at the GGA level.<sup>358</sup> The DFT+U method (Section 7.3.1) showed improvement in the description of the band structure<sup>212</sup> and electron dynamics.<sup>213</sup> The "exact exchange for correlated electrons" (EECE) method<sup>359,360</sup> improved magnetic moments and band gaps in transition-metal monoxides through the functional form nearly identical to (7.17), but only applied to the *d*-orbitals. All those atomic correction methods were introduced in the *ad hoc* manner and always involved empirical parameters. On the other hand, the expression (7.17) represents a first-of-akind, systematically derived atomic correction scheme, which is *totally nonempirical*, as we will show below.

# 7.4.3 Atomic Self-interaction Correction (DFT+JJ)

To proceed from (7.17), we first recognize that any exact exchange energy can be decomposed into the self-exchange energy, which corrects electrostatic selfinteraction (Section 6.5.4.1), and the remaining, "true" exchange energy.<sup>256</sup> This physics-based decomposition also applies to the exact exchange energy of the atom A  $(E_x[\gamma_{\Gamma_{dis,A}}]$  in (7.17)), which is viewed as an independent reference system in our regional hybrid formalism (Section 7.4.1). We first note that<sup>326</sup>

$$E_{x}[\gamma_{\Gamma_{dis,A}}] = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \rho_{\mu\nu,A} \rho_{\lambda\sigma,A} \langle \varphi_{\mu,A} \varphi_{\lambda,A} | \varphi_{\sigma,A} \varphi_{\nu,A} \rangle$$
(7.18)

Here  $\varphi_{i,A}$  are valence orbitals of the free atom A, and  $\rho_{\mu\nu,A}$  are the atomic density matrix elements, related to the atomic electron density as

$$\rho_{\Gamma_{dis,A}}(\mathbf{r}) = \sum_{i} \sum_{\mu,\nu} f_i C^i_{\mu,A} C^i_{\nu,A} \varphi_{\mu,A}(\mathbf{r}) \varphi_{\nu,A}(\mathbf{r})$$

$$\rho_{\Gamma_{dis,A}}(\mathbf{r}) = \sum_{\mu,\nu} \rho_{\mu\nu,A} \varphi_{\mu,A}(\mathbf{r}) \varphi_{\nu,A}(\mathbf{r})$$

$$\rho_{\mu\nu,A} = \sum_{i,\mu,\nu} f_i C^i_{\mu,A} C^i_{\nu,A}$$
(7.19)

Density matrix elements  $\rho_{ij,A}$  are obtained by projecting one-electron Kohn-Sham wavefunctions onto atomic  $\varphi_{i,A}$  and  $\varphi_{j,A}$  orbitals only within the projection sphere, centered on the atom A, as implemented in VASP in the context of the DFT+U method.<sup>361</sup> The first equation in (7.19) is identical to (7.7).

Diagonalization of the matrix  $\rho_{ij}$  to form  $(\rho')_{ij} = \rho'_{ij}\delta_{ij}$  by means of the unitary transformation converts (7.18) to

$$E_{x}[\gamma_{\Gamma_{dis,A}}] = \frac{1}{2} \sum_{\mu} \rho'_{\mu\mu,A} \rho'_{\mu\mu,A} \langle \varphi'_{\mu,A} \varphi'_{\mu,A} | \varphi'_{\mu,A} \varphi'_{\mu,A} \rangle + \frac{1}{2} \sum_{\substack{\mu\lambda\\\mu\neq\lambda}} \rho'_{\mu\mu,A} \rho'_{\lambda\lambda,A} \langle \varphi'_{\mu,A} \varphi'_{\lambda,A} | \varphi'_{\lambda,A} \varphi'_{\mu,A} \rangle = E_{x}^{1} + E_{x}^{2}$$

$$(7.20)$$

Here  $\varphi'_{\mu}$  are atomic eigenfunctions of the basis set, in which the matrix  $\rho_{ij}$  is diagonal. The two groups of terms in (7.20) (denoted as  $E_x^1$  and  $E_x^2$ ) correspond to the selfexchange and the "true" (2-electron) exchange in the free-atom reference system, as described above. To incorporate this fundamental exchange energy separation into the regional hybrid functional formalism (7.17), we take a step back and separate the group of  $N_A$  atomic basis set functions  $\Gamma_{dis,A}$  into  $N_A$  groups  $\Gamma_{i,A}^1$  containing 1 orbital each, and repeat the derivation of the regional hybrid functional. (7.17) then becomes:

$$E_{xc}[\rho] = E_{xc}^{sl}[\rho] + \sum_{A} \left( \sum_{i=1}^{i=N_a} \frac{1}{n_{\Gamma_{i,A}^{1}}} \left[ E_x \left[ \gamma_{\Gamma_{i,A}^{1}} \right] - E_x^{sl} \left[ \rho_{\Gamma_{i,A}^{1}} \right] \right] + \frac{1}{n_{int,A}} \left[ E_x \left[ \gamma_{int,A} \right] - E_x^{sl} \left[ \rho_{int,A} \right] \right] \right)$$
(7.21)

The first term in parentheses in (7.21) sums over terms, each defined over a single basis set orbital  $\varphi'_{i,A}$  in  $\Gamma^1_{i,A}$ ;  $E_x \left[ \gamma_{\Gamma^1_{i,A}} \right]$  is identical to a single term in the first summation in (7.20). The second term involves products of distinct basis set functions  $\varphi'_{i,A}$  and  $\varphi'_{j,A}$ ;  $E_x \left[ \gamma_{int,A} \right] \equiv E_x^2$ . In a direct analogy with (7.10), (7.21) is identical to

$$E_{xc}[\rho] = \sum_{A} \left( \sum_{i=1}^{i=N_a} E_{xc} \left[ \rho_{\Gamma_{i,A}^1} \right] + E_{xc}[\rho_{int,A}] \right) + E_{xc}[\rho_{\Gamma_{cont}}]$$
(7.22)

To simplify (7.21), we first note that in the semiclassical  $Z \to \infty$  limit, where Z is a nuclear charge and a number of electrons in neutral atoms, the semilocal DFT theory becomes exact (the atom is so large that density variations are small) with the second-order gradient expansion coefficient  $\mu_{2GE}^{exact}$  of 0.260.<sup>362</sup> The corresponding coefficient of the PBE functional is close to that value ( $\mu_{2GE}^{PBE} = 0.21951$ ).<sup>14</sup> Since the number of electron pairs scales as  $Z^2$  at large Z, and the number of singles trivially scales as Z, at the  $Z \to \infty$  limit the contribution of the self-exchange into the total exact exchange energy ( $E_x^1$  in (7.20)) shall become negligible, in comparison to the "true" 2-electron exchange  $E_x^2$ . Therefore, the similarity of  $\mu_{2GE}^{exact}$  and  $\mu_{2GE}^{PBE}$  implies that PBE is a good statistical approximation specifically to  $E_x^2$ . The numerical difference between the coefficients is inconsequential due to the error cancellation between exchange and correlation – the correlation part of PBE is designed to cancel  $\mu_{2GE}^{PBE}$  exactly at low generalized density gradients, in order to reproduce the spin-polarized LDA (LSDA), which is more accurate at small gradients.<sup>14</sup> Therefore,  $E_{xc}^{PBE}[\rho_{int,A}]$  is a very accurate statistical approximation to  $E_{xc}^{exact}[\rho_{int,A}]$ , even at small Z – a combination of the nonlocal exchange and the nonlocal correlation holes (see Section 6.5.1) yields a much more local exchange-correlation hole, described well by semilocal DFT methods, such as PBE. We conclude that the  $E_{xc}[\rho_{int,A}]$  term in (7.22) should *not* be corrected by the regional hybrid, and hence the last term in (7.21) can be dropped.

How well does the statistical approximation work for  $E_{xc} \left[ \rho_{\Gamma_{i,A}^{1}} \right]$  in (7.22)? The  $\Gamma_{i,A}^{1}$  contains one atomic orbital, and thus in the limit of one atom,  $E_{xc} \left[ \rho_{\Gamma_{i,A}^{1}} \right]$  describes exchange-correlation effects in a one-electron reference system. This is equivalent to Z=1, and thus the statistical approximation shall break down. In addition, exact correlation vanishes for any 1-electron system (correlation is a 2-electron phenomenon). Although it does not vanish in PBE due to the self-correlation error, it is small (-0.18 eV in a H atom vs. -1 ...-2 eV exact correlation energy between 1 electron and all other electrons;<sup>273</sup> the actual value is weakly sensitive to the number of electrons in an atom). We conclude that there is no significant error cancellation in  $E_{xc} \left[ \rho_{\Gamma_{i,A}^{1}} \right]$ , unlike in  $E_{xc} \left[ \rho_{int,A} \right]$ ; its corresponding exact exchange-correlation hole

remains non-local and poorly described by PBE, necessitating the regional hybrid correction. Therefore, the second term in (7.21) should be retained.

In (7.21), *n* corresponds to the highest order of the perturbation theory (PT), which allows for the accurate description of correlation effects in the system. The lowest PT order that yields the correlation energy is 2 (see (6.69)); since 1-electron correlation is formally zero,  $n_{\Gamma_{l,A}^1}$  equals 1, i.e., it is equal to the formal order of the Hartree-Fock theory,<sup>256</sup> which describes the self-exchange exactly. Therefore, (7.21) becomes

$$E_{xc}[\rho] = E_{xc}^{sl}[\rho] + \sum_{A} \sum_{i=1}^{i=N_a} \left( E_x \left[ \gamma_{\Gamma_{i,A}^1} \right] - E_x^{sl} \left[ \rho_{\Gamma_{i,A}^1} \right] \right)$$
(7.23)

The expression (7.23) is essentially identical to DFT-SIC by Perdew and Zunger (6.60) in the atomic limit (since  $U = -E_x$  for 1-electron systems) – it corrects the SIE in atoms. The only difference is that  $E_x^{sl}$  and  $E_x$  are evaluated for non-self-consistent, spherical, non-spin-polarized atomic densities, for which  $\Gamma_{i,A}^1$  basis sets have been initially generated in VASP. This subtle difference is extremely important for eliminating DFT-SIC drawbacks, as we will illustrate in the next section.

Next, we simplify (7.23) by taking advantage of the atomic basis set transferability across all conceivable chemically bonded structures. The exact selfexchange is

$$E_{x}\left[\gamma_{\Gamma_{i,A}^{1}}\right] = \frac{1}{2}\rho_{ii,A}^{\prime}\rho_{ii,A}^{\prime}\left\langle\varphi_{i,A}^{\prime}\varphi_{i,A}^{\prime}\right|\varphi_{i,A}^{\prime}\varphi_{i,A}^{\prime}\right\rangle = -J_{i,A}^{ex}o_{i,A}^{2}$$
(7.24)

Here  $o_i = \rho'_{ii,A}$  is an orbital occupancy, i.e., the probability of finding an electron in the atomic orbital *I* in the atom *A*. It is an eigenvalue of the density matrix  $\rho_A$  (7.19).  $E_x \left[ \gamma_{\Gamma_{i,A}^1} \right] = -J_{i,A}^{ex}$  for  $o_i = 1$ , i.e.,  $J_{i,A}^{ex}$  is the exact self-exchange in the atomic orbital in the limit of a free atom. The semilocal self-exchange in the GGA approximation (see also (6.40)) is

$$E_{x}^{sl}\left[\rho_{\Gamma_{i,A}^{1}}\right] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int F_{x}(s(\mathbf{r})) \rho_{\Gamma_{i,A}^{1}}^{4/3}(\mathbf{r}) d\mathbf{r}$$
(7.25)

At the beginning of this section, we mentioned that the projection region  $\Omega_A$ , to which the regional hybrid correction is applied in (7.23), coincides with the augmentation sphere for the majority of atoms in the PAW method; its radius is

evidently smaller than the atomic one to ensure that neighboring spheres do not overlap, and is roughly equal to the ionic radius of the atom A. Therefore, atomic tail regions lie outside Ω<sub>A</sub>, and the most energetically relevant range of generalized gradient values is roughly  $0 \le s \le 1$  (does not apply to s-elements; vide infra).<sup>363</sup> In this range, we can approximate the



Figure 7.6. Dimensionless exchange enhancement factor F(s) as a function of the dimensionless squared generalized gradient  $s^2$ . The fitting by the binomial (6.26) is shown in red.

exchange enhancement factor (6.47) of the PBE functional with very good accuracy ( $R^2$ =0.9957) by the following binomial (Figure 7.6):

$$F_{x}(s(\mathbf{r})) = 1.0041 + 0.1752s^{2} \tag{7.26}$$

We modify the generalized gradient expression (6.39) as follows:

$$s = \frac{1}{2(3\pi^2)^{1/3}} \times \frac{|\nabla \rho|}{\rho^{4/3}} = \frac{1}{2(3\pi^2)^{1/3}} \rho^{-2/3} \frac{\nabla \rho}{\rho^{2/3}} =$$

$$= \frac{3}{2(3\pi^2)^{1/3}} \rho^{-2/3} \nabla (\rho^{1/3})$$
(7.27)

After substituting (7.27) into (7.26), and then (7.26) into (7.25), we obtain

$$E_{x}^{sl}\left[\rho_{\Gamma_{l,A}^{1}}\right] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \left(1.0041 + 0.1752 \frac{9}{4(3\pi^{2})^{2/3}} \rho_{\Gamma_{l,A}^{1}}^{-4/3} \left(\nabla\left(\rho_{\Gamma_{l,A}^{1}}^{1/3}\right)\right)^{2}\right) \rho_{\Gamma_{l,A}^{1}}^{4/3} d\mathbf{r}$$

$$(7.28)$$

(7.28) can be split into LDA and GGA contributions:

$$E_{x}^{sl}\left[\rho_{\Gamma_{l,A}^{1}}\right] = -1.0041 \times \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \rho_{\Gamma_{l,A}^{1}}^{4/3} d\mathbf{r}$$

$$- 0.0412 \times \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \left(\nabla\left(\rho_{\Gamma_{l,A}^{1}}^{1/3}\right)\right)^{2} d\mathbf{r}$$
(7.29)

Since 
$$\rho_{\Gamma_{i,A}^1}(\mathbf{r}) = \rho'_{ii,A} \varphi'_{i,A}(\mathbf{r}) \varphi'_{i,A}(\mathbf{r}) = o_{i,A} \varphi'_{i,A}(\mathbf{r}) \varphi'_{i,A}(\mathbf{r})$$
 from (7.19),

(7.29) together with (7.24) and (7.23) become

$$E_{xc}[\rho] = E_{xc}^{sl}[\rho] + \sum_{A} \sum_{i=1}^{i=N_a} \left( -J_{i,A}^{ex} o_{i,A}^2 + J_{i,A}^{LDA} o_{i,A}^{4/3} + J_{i,A}^{GGA} o_{i,A}^{2/3} \right)$$
(7.30)

Here  $J_{i,A}^{LDA}$  and  $J_{i,A}^{GGA}$  correspond to LDA and GGA energies of a single orbital in a free atom A. It should be noted that all  $J_i$  parameters are defined in terms of a single basis set orbital  $\varphi'_{i,A}$  and thus are fully transferable across all bonded structures. They need to be calculated only once, making the method extremely computationally efficient.

Next, we simplify (7.30) and introduce the effective exponent *k*:

$$E_{xc}[\rho] = E_{xc}^{sl}[\rho] + \sum_{A} \sum_{i=1}^{i=N_a} \left( J_{i,A}^{sl} o_{i,A}^k - J_{i,A}^{ex} o_{i,A}^2 \right)$$
(7.31)

The PW91 functional, which yields energies nearly identical to PBE, is very accurate for free atoms, with exchange-correlation (XC) energy errors <0.15 eV/electron.<sup>273</sup> Therefore, the regional hybrid ("JJ") correction should be zero identically in the free atom limit. According to (7.31), this requires two conditions to be met for all *i* in free atoms A: (1)  $J_{i,A}^{sl} = J_{i,A}^{ex}$ , and (2)  $o_{i,A} = 1$ . In section 7.4.5 we show that condition 1 is met for a H atom to a very good accuracy (0.02 eV error), and thus it is also met for other group 1 and group 11 atoms with slower varying *s*-densities in comparison with H. Condition 2 requires non-overlapping projection spheres  $\Omega_A$  to contain an integer number of electrons. This is satisfied for standard augmentation radii  $R_{\text{ionic}}$  for nearly all elements, except for monovalent group 1 and group 11 elements. For, if  $R_{\Omega} < R_{\text{atom}}$ , then a particular *s* orbital contains either a fractional or 0 number of electrons, in violation of the condition 2. To avoid this, we relax the nonoverlapping sphere requirement for s elements and set  $R_{\Omega_A} = R_{A,\text{atom}}$ . We find this does not affect the method performance.

In this section, we derived the atomic self-interaction correction formula (7.31) from the general notion of the regional hybrid functional. Next, we will provide arguments for the choice of a particular *k* exponent value from the general properties of atomic electron densities.

## 7.4.4 Z-representability

In the Hohenberg-Kohn DFT theory, the key requirement for an electron density is that it must be *v*-representative, i.e., there exists an external potential  $v(\mathbf{r})$ ,

which generates the antisymmetric many-electron wave function and its corresponding density.<sup>257</sup> Space of potentials is allowed to be constrained by symmetry via the set of observables, e.g., quantum numbers, which the system exhibits.<sup>364</sup> As a result, the electron densities are also constrained.

It is evident that such constraints exist for one-electron densities  $\rho_{\Gamma_{i,A}^1}$  of reference atoms that enter the DFT+JJ expression (7.32). The angular shape of every orbital  $\varphi'_{i,A}$  in the  $\Gamma_{i,A}^1$  group is fixed by well-defined azimuthal (1s, 2p, etc.) and magnetic (p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub>) quantum numbers. The radial shape of  $\varphi'_{i,A}$  is also fixed, since the orbital is calculated for a spherical, non-polarized free atom, and thus there is only one external potential  $v(\mathbf{r})$  that generates it. Such strict constraints introduce a serious conceptual difficulty for generation of a JJ term contribution to the Kohn-Sham oneelectron potential. The latter requires the variational principle (7.30) to hold, i.e.,  $E[\rho_0] < E[\rho_0 + \delta\rho]$ , whereas constraints require that  $\delta\rho = 0$ . We restore the variational space and derive a JJ contribution to the potential by relaxing certain constraints.

$$E_{xc}[\rho] = E_{xc}^{sl}[\rho] + \sum_{A} \sum_{i=1}^{i=N_a} \left( E_x \left[ \gamma_{\Gamma_{i,A}^1} \right] - E_x^{sl} \left[ \rho_{\Gamma_{i,A}^1} \right] \right)$$
(7.32)

First, we note that angular constraints cannot be relaxed, since spherically symmetric atoms possess a centrally symmetric field, and thus angular momentum is conserved.<sup>255</sup> Therefore, it is the radial constraints that have to be lifted.

In non-spin-polarized atoms, the radial electron density distribution is described well by piecewise exponential functions, such that each value of the exponent corresponds to a particular electronic shell.<sup>365</sup> Exponentially decaying

densities are produced by the Slater form of the radial function, associated with a particular atomic orbital:<sup>366</sup>

$$\varphi_{i,A}(r) = (2Z)^n \sqrt{\frac{2Z}{(2n)!}} r^{n-1} e^{-Zr}$$
(7.33)

Here Z is an effective nuclear charge, screened by other electrons, and n is a principal quantum number. (7.33) does not account for radial nodes, present in true atomic orbitals – they are shown to be close to the nucleus and unimportant.<sup>367</sup> Also, nodes are naturally neglected in the pseudopotential method, such as PAW. Hartree-Fock calculations indicate<sup>368</sup> that (7.33) is an excellent approximation to the radial orbital part, provided that Z is optimized for each orbital.

The universality of (7.33) suggests relaxing radial constraints by introducing the following ansatz: we *assume* that the variational space of all possible single-orbital radial densities of reference atoms is constrained by the Slater orbital form (7.33) with all possible values *Z*. We refer to such densities as *Z*-representable.

The GGA approximation to  $E_{xc}$  depends on two ingredients – the density and its gradient. Since the space of Z-representative densities has only one degree of freedom (Z), density variations due to the Z change will lead to *correlated* variations of LDA and GGA contributions to  $E_{xc}$ . To show this, we consider the case of n=1 (a hydrogen atom) and assume that the orbital density is Z-representable. The expression (7.33), multiplied by normalized spherical harmonics, is

$$\varphi_{i,A}(r) = \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Zr}$$
(7.34)

Assuming that the model (7.29) holds, the LDA part becomes

$$E_x^{LDA}[\rho_H] = -1.0041C_{LDA}\frac{4}{\pi^{1/3}}Z^4 \int e^{-\frac{8}{3}Zr}r^2 dr = -0.2892C_{LDA}Z$$
(7.35)

The GGA part is

$$E_{x}^{GGA}[\rho_{H}] = -0.0412 \times \frac{16\pi^{1/3}}{9} Z^{4} C_{LDA} \int e^{-\frac{4}{3}Zr} r^{2} dr = -0.0905 C_{LDA} Z$$
(7.36)

It is evident that, within the space of Z-representable densities, the GGA part is linearly proportional to the LDA exchange. Therefore, the effect of GGA amounts to multiplication of the LDA exchange by a constant, i.e., (7.25) becomes

$$E_x^{sl}\left[\rho_{\Gamma_{i,A}^1}\right] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} F_x \int \rho_{\Gamma_{i,A}^1}^{4/3}(\mathbf{r}) d\mathbf{r}$$
(7.37)

For a hydrogen atom, we find  $F_x = 1.313$ . Obviously, this value is too high, since the model (7.29) only holds for  $0 \le s \le 1$ , whereas in (7.36) we performed integration until  $s \to \infty$ . To obtain a more realistic constant value, we used the full expression for the exchange enhancement factor (7.47) and performed the numerical integration. The result is  $F_x = 1.1939$ , totally independent of the Z value. In Table 7.6, we report  $F_x$  for various principal quantum numbers. Remarkably, the values vary slightly and are also independent of Z for all quantum numbers. This suggests that the self-exchange in atomic orbitals is universally described by the modified LDA theory (7.37).

Ν	$F_x$
1	1.1939
2	1.1756
3	1.1798
4	1.1867
5	1.1930

 Table 7.6. Computed constant exchange enhancement factors as a function of a principal quantum number

Our result is consistent with the work of Perdew and co-workers<sup>369</sup>, who have shown that the exchange hole for 1- and 2-electron systems is surprisingly local, and the modified LDA theory (LDSA0) applies with  $F_x = 1.174$ , which is remarkably close to our (PBE) value 1.1939. The exact constraint is  $F_x \leq 1.174$ ;<sup>301</sup> our value violates it, which is likely due to the deficiencies of the PBE functional form. Moreover, Lindgren and Schwarz<sup>370</sup> showed in 1972 that the exchange-only LDA (Dirac exchange) reproduces Hartree-Fock self-exchange in atomic orbitals, when it is multiplied by the constant  $F_x$ , which varies weakly across the Periodic Table. The values they found are  $\approx 1.16$  for 1s, 2p, and 3d; 1.09-1.15 for 2s, 3s, and 3p for elements up to Kr. Again, this is consistent with our finding of LDA universality for self-exchange energies of Z-representable densities.

From (7.37) it follows that k can be set to the universal constant 4/3 for all orbitals and all atoms in (7.31). The resulting expression is

$$E_{xc}[\rho] = E_{xc}^{sl}[\rho] + \sum_{A} \sum_{i=1}^{i=N_a} \left( J_{i,A}^{sl} o_{i,A}^{4/3} - J_{i,A}^{ex} o_{i,A}^2 \right) \Big|_{J_{i,A}^{sl} = J_{i,A}^{ex}}$$
(7.38)

This concludes the derivation of the DFT+JJ theory. Contrary to our original empirical hypothesis that the JJ correction should only be applied to p and d orbitals, the generality of (7.38) suggests that it shall work with s electrons too. In the next section, we will test the method performance for the simplest quantum mechanical

systems – group 1 and group 11 free atoms with 1 s valence electron. We will introduce a theorem that enables a remarkably simple calculation of the J parameter and will assess the DFT+JJ performance in predictions of ionization energies of atoms.

#### 7.4.5 Free Monovalent Atoms

In a singly occupied s orbital, the JJ correction vanishes, since  $1^{4/3} - 1^2 = 0$ . Therefore, the DFT+JJ will not affect total energies of atoms, which are already accurate at the GGA level of theory. However, it will affect Kohn-Sham eigenvalues, which are the DFT analogs of molecular orbital energies.

The DFT analog of the Koopman's theorem associates the highest occupied orbital eigenvalue with negative of the ionization energy of a finite system, provided that the DFT functional is exact:<sup>257</sup>

$$\varepsilon_{HOO} = -I \tag{7.39}$$

This equality does not hold for semilocal functionals due to the manyelectron SIC (Section 6.5.4.1, Figure 6.1), which results in downward energy deviations from the piecewise linearity for fractional electron numbers. Since the JJ term in (7.39) is positive for fractional atomic orbital occupancies (Figure 7.7), it will offset those deviations and can eliminate SIC. If the



Figure 7.7. Energy penalty terms in DFT+JJ and DFT+U theories. Parameter values are taken as unity.

system is SIC-free, then (7.39) should hold, and the highest Kohn-Sham eigenvalue should be equal to the experimentally measured ionization energy. We will test this hypothesis for s-elements in a free atom form (H, Li, Na, K, Rb, Cs, Fr, Cu, Ag, Au).

The highest occupied Kohn-Sham orbital (HOO) eigenvalue is

$$\varepsilon_{HOO} = \left\langle \varphi_{HOO} \middle| -\frac{1}{2} \nabla^2 + v_{es} + v_{xc} \middle| \varphi_{HOO} \right\rangle \tag{7.40}$$

Here  $\varphi_{HOO}$  is the HOO,  $v_{es}$  is the electrostatic potential due to nuclei-electron and classical electron-electron interactions, and  $v_{xc}$  is the exchange-correlation potential. For a single s orbital, in which the density matrix eigenvalue coincides with the actual orbital occupancy, we can express the potential as

$$v_{xc,s} = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta E_{xc}^{sl}[\rho]}{\delta \rho(\mathbf{r})} + J\left(\frac{4}{3}o_s^{1/3} - 2o_s\right)$$
(7.41)

The HOO eigenvalue is then

$$\varepsilon_{HOO,s} = \left\langle \varphi_{HOO,s}' \Big| -\frac{1}{2} \nabla^2 + v_{es} + v_{xc}^{sl} \Big| \varphi_{HOO,s}' \right\rangle + \left\langle \varphi_{HOO,s}' \Big| J_s \left( \frac{4}{3} o_s^{1/3} - 2o_s \right) \Big| \varphi_{HOO,s}' \right\rangle$$
(7.42)

We integrate the orbital out in the second term in (7.42) and obtain

$$\varepsilon_{HOO,s} = \varepsilon_{HOO,s}^{sl} + J_s \left(\frac{4}{3}o_s^{1/3} - 2o_s\right)$$
(7.43)

Here  $\varepsilon_{HOO,s}^{sl}$  is the HOO eigenvalue, obtained at the semilocal theory level, but for an DFT+JJ-optimized orbital  $\varphi_{HOO,s}'$ . We find that relaxations are described well by the semilocal theory, so that equation (7.43) can be applied non-self-consistently.

For the free atoms of s-elements with  $o_s = 1$ , (7.43) becomes very simple:

$$\varepsilon_{HOO,s} = \varepsilon_{HOO,s}^{sl} - \frac{2}{3}J_s \tag{7.44}$$

In Table 7.7, we report  $J_s$ ,  $\varepsilon_{HOO,s}^{sl}$ ,  $\varepsilon_{HOO,s}$ , and experimental ionization energies for Li and Na. There are PAW pseudopotentials available for those elements that contain 1 valence s electron, simplifying  $J_s$  parameter extraction. For Li and Na, it turned out to be impossible to extract  $J_s$  at the DFT level directly due to compensation charge complications in the PAW method. Therefore,  $J_s$  was obtained at the Hartree-Fock level of theory for a frozen orbital.  $J_s$  was identified with the plane wave part of the exact exchange.

Table 7.7. Comparison of PBE and PBE+JJ HOO eigenvalues with experimental ionization energies for Li and Na

Free atoms	$J_s$ , eV	$\varepsilon^{PBE}_{HOO,s}$ , eV	$\varepsilon_{HOO,s}^{PBE+JJ}$ , eV	- <i>I</i> , eV
Li	-3.18	-3.27	-5.39	-5.39
Na	-3.01	-3.0584	-5.0651	-5.14

The agreement with the experiment is excellent, indicating that, indeed, DFT+JJ corrects many-electron self-interaction error, and the choice of the universal exponent 4/3 is optimal.

The pseudopotentials of elements other than Li and Na (H is considered later) treat both *s* states and *p* semicore states as valence states, and thus the extraction of  $J_s$  of a single *s* orbital would require significant VASP code modifications. Fortunately, we discovered a theorem that allows one to extract  $J_s$  from atomic eigenvalues.

**Theorem.** For Z-representable densities of singly occupied atomic s orbitals, the following identity holds at the spin-polarized GGA level of theory:
$$J_{s} = -E_{xc}[\rho_{s,\uparrow}] = \varepsilon_{s,\downarrow} - \varepsilon_{s,\uparrow}$$
(7.45)

Here  $E_{xc}[\rho_{\uparrow,s}]$  is the self-exchange energy of the majority spin s-orbital, which includes the self-correlation error.  $\varepsilon_{\uparrow,s}$  and  $\varepsilon_{\downarrow,s}$  are the majority-spin and minorityspin s orbital eigenvalues. The  $\varepsilon_{\uparrow,s}$  is computed for a fixed orbital and a potential, which correspond to the non-spin-polarized reference atom; the  $\varepsilon_{\downarrow,s}$  is computed selfconsistently, but at the fixed electrostatic potential of the non-spin-polarized reference atom.

## Proof for an H atom.

In a non-spin-polarized H,

$$\varepsilon_s = \left\langle \varphi_s \left| -\frac{1}{2} \nabla^2 + v_{es}[\rho_s] + v_{xc}[\rho_s] \right| \varphi_s \right\rangle \tag{7.46}$$

Here  $\rho_s(\mathbf{r}) = \varphi_s^2(\mathbf{r})$ . At  $r \to \infty$ ,  $\varphi_s \to e^{-Zr}.^{371}$  The asymptotic decay of the PBE  $v_{xc}$  is exponential. For the B88 functional,  $v_{xc} \to -\frac{5}{4Zr^2}.^{371}$ . PBE and B86 share a similar functional form of the exchange enhancement factor and thus both experience asymptotic potential decay. B86 and B88, however, yield almost identical potential tails in the energetically relevant regions of atoms and produce very similar atomic Kohn-Sham eigenvalues.<sup>371</sup> Because of this similarity, we approximate the PBE exponential decay with a more computationally convenient  $v_{xc}[\rho_s] \to -\frac{5}{4Zr^2}$ .

At large, but energetically relevant r, the following asymptotic Kohn-Sham equation should hold:

$$\left(-\frac{1}{2}\nabla^{2} + v_{es}[\rho_{s}] - \frac{5}{4Zr^{2}}\right)e^{-Zr} = \varepsilon_{s}e^{-Zr}$$
(7.47)

If  $\varphi_s$  is Z-representable, then it has the same exponent Z in the entire range  $0 \le r < \infty$ . The exponential shape of the density and thus of the orbital is found to be universal and insensitive to the actual form of the Hamiltonian, even when drastic approximations about the kinetic and/or exchange energy are made.<sup>365</sup> Therefore, we *assume* that  $\varphi_s \sim e^{-Zr}$  even when the domain of the asymptotic potential  $-\frac{5}{4Zr^2}$  is artificially extended to  $0 \le r < \infty$  ("status quo ansatz"). Of course, this is just a mathematical construction, since the actual  $v_{xc}$  does not resemble the asymptotic one in the regions of high electron density.

According to the spin-scaling relationship,<sup>372</sup> obeyed by the PBE functional, the exchange energy of a spin-polarized singly occupied orbital is related to the nonspin-polarized one as

$$E_x[\rho_s, 0] = \frac{1}{2} E_x[2\rho_s]$$
(7.48)

Since the asymptotic decay of the potential does not depend on the density explicitly, we conclude that

$$v_{xc}[\rho_s, 0] = \frac{1}{2} v_{xc}[\rho_s] = -\frac{5}{8Zr^2} \text{ at large } r$$
 (7.49)

When the spin polarization is turned on, the  $\varepsilon_s$  is split into lower lying, occupied majority spin  $\varepsilon_{s,\uparrow}$  and higher lying, unoccupied minority spin orbital  $\varepsilon_{s,\downarrow}$  energies. Assuming the artificially extended *r*-domain for the asymptotic potential, the following Kohn-Sham equations hold:

$$\left(-\frac{1}{2}\nabla^{2} + v_{es}[\rho_{s}] - \frac{5}{8Zr^{2}}\right)|\varphi_{s,\uparrow}\rangle = \varepsilon_{s,\uparrow}|\varphi_{s,\uparrow}\rangle$$

$$\widehat{H}_{\uparrow}|\varphi_{s,\uparrow}\rangle = \varepsilon_{s,\uparrow}|\varphi_{s,\uparrow}\rangle$$

$$(7.50)$$

$$\left( -\frac{1}{2} \nabla^2 + v_{es}[\rho_s] \right) |\varphi_{s,\downarrow}\rangle = \varepsilon_{s,\downarrow} |\varphi_{s,\downarrow}\rangle$$

$$\widehat{H}_{\downarrow} |\varphi_{s,\downarrow}\rangle = \varepsilon_{s,\downarrow} |\varphi_{s,\downarrow}\rangle$$

$$(7.51)$$

Since the energy difference between  $\varepsilon_{s,\uparrow}[\varphi_{s,\uparrow}]$  and  $\varepsilon_{s,\uparrow}[\varphi_s]$  is only 0.04 eV at fixed  $v_{es}[\rho_s]$ , we assume  $\varphi_{s,\uparrow} = \varphi_s \sim e^{-Zr}$  to simplify the analysis that follows. According to the integral version of the Hellmann-Feynman theorem,<sup>257</sup>

$$\varepsilon_{s,\downarrow} - \varepsilon_{s,\uparrow} = \frac{\langle \varphi_{s,\uparrow} | \hat{H}_{\downarrow} - \hat{H}_{\uparrow} | \varphi_{s,\downarrow} \rangle}{\langle \varphi_{s,\uparrow} | \varphi_{s,\downarrow} \rangle} = \frac{\langle \varphi_{s,\uparrow} | \frac{5}{8Zr^2} | \varphi_{s,\downarrow} \rangle}{\langle \varphi_{s,\uparrow} | \varphi_{s,\downarrow} \rangle}$$
(7.52)

For a hydrogen atom, we find that  $\varepsilon_{s,\downarrow}=+0.01$  eV. Since the  $\hat{H}_{\downarrow}$  Hamiltonian resembles that of an electron in a He atom in the Hartree-Fock theory,  $\varphi_{s,\downarrow}$  can be taken as Zrepresentable, i.e.  $\varphi_{s,\downarrow} \sim e^{-Z'r}$ . However, at large  $r \varphi_{s,\downarrow} \sim e^{-(-2\varepsilon_{s,\downarrow})^{1/2}r}$ .<sup>257</sup> Since  $\varepsilon_{s,\downarrow} \approx$ 0,  $\varphi_{s,\downarrow}$  is nearly constant, and thus it can be taken outside integrals in (7.52) and cancelled out. (7.52) becomes

$$\varepsilon_{s,\downarrow} - \varepsilon_{s,\uparrow} = \frac{\int_0^\infty \frac{5}{8Zr^2} r^2 e^{-Zr}}{\int_0^\infty r^2 e^{-Zr}} = \frac{5}{8Z} \frac{Z^{-1}}{2Z^{-3}} = \frac{1}{2} \times \frac{5Z}{8}$$
(7.53)

The  $\frac{5Z}{8}$  is, however, the electrostatic energy between 2 electrons occupying the same *s* orbital, e.g., in a He atom.<sup>255</sup> Therefore,  $\frac{1}{2} \times \frac{5Z}{8}$  is the self-interaction energy of an *s* electron. Since the PBE functional produces accurate exchange energies of atoms, we have

$$\varepsilon_{\mathsf{s},\downarrow} - \varepsilon_{\mathsf{s},\uparrow} = \frac{1}{2} \times \frac{5Z}{8} = U[\rho_s] \approx -E_{xc}[\rho_{\mathsf{s},\uparrow}] = J_s \tag{7.54}$$

Q.E.D.

#### In Table 7.8, we report numerical tests for H, Li, and Na:

Free atoms	ε <sub>s,↑</sub> , eV	$\varepsilon_{s,\downarrow}, eV$	$\varepsilon_{\rm s,\downarrow} - \varepsilon_{\rm s,\uparrow},  {\rm eV}$	$J_s$ , eV
Н	-7.8924	+0.0100	-7.9024	-7.9012
Li	-3.26	-0.09	-3.17	-3.18
Na	-3.0547	-0.0813	-2.9734	-3.0099

Table 7.8. Comparison between left-hand and right-hand parts of (7.55)

The agreement is impressive – the theorem is numerically supported.

We note that  $\varepsilon_{s,\uparrow}$  was calculated at the frozen orbital and frozen electrostatic potential, pre-calculated for a non-spin-polarized atom. To obtain  $\varepsilon_{s,\downarrow}$ , we performed orbital relaxation at the same frozen electrostatic potential for H and Li. A slightly different procedure was used for Na. Originally, we found its  $\varepsilon_{s,\downarrow}$  to be too negative (-1.36 eV), which is contrary to expectations, since  $\varepsilon_{s,\downarrow}(Na)$  is expected to be higher in energy than  $\varepsilon_{s,\downarrow}(H)$  due to the lower experimental electron affinity of the former. Too negative  $\varepsilon_{s,l}(Na)$  is probably related to the "ghost state" problem of certain PAWs.<sup>48</sup> To circumvent this, we optimized  $\varphi_{s,\downarrow}$  at the Hartree-Fock level of theory at the fixed electrostatic potential, followed by PBE calculation of  $\varepsilon_{s,\downarrow}(Na)$  for the frozen orbital and the potential. Importantly, both Hartree-Fock and DFT produce near zero values of  $\varepsilon_{s,\downarrow}$  in H and Li, justifying this procedure. For Li and Na,  $J_s$  was obtained at the Hartree-Fock level of theory, as discussed previously. For H, we included the erroneous self-correlation as part of the self-exchange, since it yields a nearly perfect agreement with the exact self-exchange (-7.89 eV), presumably due to the error cancellation (-7.90 eV for XC vs. -7.74 eV for X).  $J_s$  was identified with the plane wave part of the  $E_{xc.}$ 

The key utility of the theorem is that it allows one to extract the  $J_s$  parameter value from the easily computable Kohn-Sham eigenvalues of free atoms. After combining (7.44) and (7.45), we get

$$\varepsilon_{\rm s,\uparrow}^{PBE+JJ} = \varepsilon_{\rm s,\uparrow}^{PBE,rel} - \frac{2}{3} \left( \varepsilon_{\rm s,\downarrow}^{PBE} - \varepsilon_{\rm s,\uparrow}^{PBE} \right) = \frac{5}{3} \varepsilon_{\rm s,\uparrow}^{PBE} - \frac{2}{3} \varepsilon_{\rm s,\downarrow}^{PBE} + \Delta \varepsilon_{rel}$$
(7.55)

Here  $\Delta \varepsilon_{rel}$  is the eigenvalue relaxation energy, defined as  $\Delta \varepsilon_{rel} = \varepsilon_{s,\uparrow}^{PBE,rel} - \varepsilon_{s,\uparrow}^{PBE}$ . Next, we test the DFT+JJ-derived expression (7.55) to see how well  $\varepsilon_{s,\uparrow}^{PBE+JJ}$  agrees with experimental ionization energies of group 1 and group 11 elements.

In Figure 7.8, we compare experimental ionization energies (IE) with theoretical ones, predicted using PBE and PBE+JJ by assuming that the Koopman's theorem (7.39)holds. PBE describes the experimental IE trend well, but consistently underestimates ionization energies, with errors increasing from 1.68 eV (Cs)



Figure 7.8. Comparison of experimental and predicted atomic ionization energies (IE) of group 1 and group 11 monovalent elements. The parity line is shown in red.

to 3.18 eV (Au) in the direction of increasing experimental IE. PBE+JJ, on the other hand, yields an excellent agreement with the experiment. Among alkali elements, the highest errors are only -0.08 eV (Na) and +0.07 eV (Fr). The errors are higher for

coinage metals: -0.64 eV (Cu), -0.27 eV (Ag), and -0.20 eV (Au). We attribute these greater errors to the fact that uncorrected *d*-states are energetically close to the *s*-state and thus may influence its energy. Indeed, *d*-*s* gaps in those elements are much narrower (~0.4-3 eV) than *p*-*s* gaps of alkali metals (~10-25 eV). It is truly remarkable that approximate PBE calculations contain all necessary information to obtain a nearly perfect agreement with the experiment using the JJ corrections!

When calculating the minority-spin  $\varepsilon_{s,\downarrow}^{PBE}$ , we encountered the same problem of too negative energies, discussed above for the Na atom. However, the solution that worked for Na, did not work for elements with *p* semicore states. We found an alternative procedure, which was based on a premise that the 2-electron exchange is described equally well by semilocal and exact methods in atoms with many electrons. We first optimized  $\varphi_{s,\downarrow}$  using PBE, and then calculated its energy using a combination of exact exchange and PBE correlation. In this case, it is unlikely that the theorem (7.45) holds, given that  $\varphi_{s,\downarrow}$  is likely localized due to its negative energy. However, there is another identity that leads to essentially the same result<sup>256</sup> – in the HF theory the energy difference between eigenvalues equals electron-electron exchange energy, provided that both orbitals have identical shape. Due to the fact that PBE describes exchange accurately, we would expect that there is a similar identity in DFT.

The hydrogen atom deserves special discussion. Its IE cannot be predicted correctly using the procedure that works for other monovalent elements. This reveals curious fundamental regularities and provides a unique opportunity to test our theory of Z-representable densities.

When (7.44) is applied to frozen *s*-orbitals of monovalent elements, the predicted  $\varepsilon_{s,\uparrow}^{PBE+JJ}$  is generally too high due to the neglect of relaxation effects. This is also the case for H – using frozen orbital energies from Table 7.8, we obtain

$$\varepsilon_{s,\uparrow} = -7.8924 - \frac{2}{3} \times 7.9024 = -13.1607 \text{ eV}$$
 (7.56)

The experimental value is much lower, -13.61 eV. After the spin polarization is turned on, the orbital relaxations lead to more contracted electron clouds with larger self-interaction and thus more negative self-exchange energies. Consequently, if the theorem (7.45) holds, such relaxations should lower the HOO eigenvalue. Indeed, eigenvalue relaxation energies  $\Delta \varepsilon_{rel}$  for all monovalent elements are negative and lie in the range -0.1...-0.2 eV. However, this is not the case for H – energy of the relaxed orbital is -7.5918 eV, so that  $\Delta \varepsilon_{rel} = +0.4$  eV. In fact, including it in (7.56) will further deteriorate the IE prediction.

A likely cause of this discrepancy is that the density of a spin-polarized H atom is no longer Z-representable. For, a more positive  $\varepsilon_{s,\uparrow}$  value means that the density is more diffuse away from the nucleus. However, overall the density is more contracted, as evident from the fact that, after relaxation, the self-exchange energy is more negative (-8.3429 vs. -7.9024 eV). This is only possible, if a single exponential function no longer describes the density distribution in a relaxed, spin-polarized H.

Since the Slater orbital (7.34) is an exact, Z-representable solution of the Schrodinger equation for H, we anticipate that restoring Z-representability of the *s* orbital should improve the IE prediction. To this end, we employ our theorem (7.45) in a reverse direction – we obtain an eigenvalue for a hypothetical Z-representative

orbital from the "self-exchange energy relaxation"  $\Delta E_{xc,\uparrow,rel}$ . This suggests the following modification of (7.55) specifically for H:

$$\varepsilon_{\mathrm{s},\uparrow}^{PBE+JJ} = \frac{5}{3}\varepsilon_{\mathrm{s},\uparrow}^{PBE} - \frac{2}{3}\varepsilon_{\mathrm{s},\downarrow}^{PBE} + \Delta E_{xc,\uparrow,rel}$$
(7.57)

After plugging the numbers into (7.57),

$$\varepsilon_{s,\uparrow}^{PBE+JJ} = \frac{5}{3}(-7.8924) - \frac{2}{3}(0.0100) + (-8.3429 + 7.9012)$$

$$= -13.6024 \text{ eV}$$
(7.58)

Remarkably, we reproduce the experimental result exactly, in a complete support of our theory!

An important prediction of the Z-representability theory is that the universal exponent 4/3 will no longer hold for non-Z-representable densities. The H atom system provides a unique opportunity to test this prediction.

We begin with the H density, optimized at the Hartree-Fock (HF) level of theory. While in the basis-set-free case it will always be Z-representable, since Hartree-Fock is the exact method for H, this is not the case in the PAW method. Inside the augmentation sphere, the shape of the atomic *s* orbital is identical to a rescaled non-spin-polarized PBE orbital, and thus has a different exponent. The PBE eigenvalue for the frozen HF PAW orbital is -7.4727 eV. The self-exchange energy is -8.4848 eV. By using (7.43), we get

$$\varepsilon_{s,\uparrow}^{PBE+JJ} = \varepsilon_{s,\uparrow}^{PBE} + J_s \left(\frac{4}{3} - 2\right) = -7.4727 - \frac{2}{3} \times 8.4848 = -13.1292 \text{ eV}$$
(7.59)

Consistent with our prediction, the value does not agree with the experimental one. Next, we generalize (7.43) as

$$\varepsilon_{\mathrm{s},\uparrow}^{PBE+JJ} = \varepsilon_{\mathrm{s},\uparrow}^{PBE} + J_s(k-2) \tag{7.60}$$

Here k is the exponent k in (7.31). For non-Z-representable densities, LDA and GGA self-exchange contributions are no longer independent. Therefore, a natural and direct way to obtain k is to multiply the system's charge distribution by a constant <1 and recalculate its self-exchange energy at the GGA level – this is equivalent to going from o = 1 to, e.g., o = 0.95 and extracting k from the effect of the occupancy change on self-exchange. We find k = 1.2805. Plugging it into (7.60), one gets

$$\varepsilon_{s,\uparrow}^{PBE+JJ} = -7.4727 + (1.2805 - 2) \times 8.4848 = -13.5775 \text{ eV}$$
 (7.61)

After we account for subtle differences between semilocal and exact J's,

$$\varepsilon_{s,\uparrow}^{PBE+JJ} = -7.4727 + 1.2805 \times 8.4848 - 2 \times 8.5050 = -13.6179 \text{ eV}$$
 (7.62)

Again, we reproduce the experimental value exactly! This result is fully consistent with our theory and indicates that, indeed, the 4/3 exponent only works for Z-representable densities and stems from the fact that GGA and LDA are correlated.

We conclude this section by considering the DFT+JJ performance for a Achilles heel of semilocal density functionals – hydrogen cation dissociation energy  $(H_2^+ \rightarrow H^{+0.5} + H^{+0.5})$ . The JJ correction increases the total energy of each atom containing 0.5 electrons by 7.9012 ×  $(0.5^{4/3} - 0.5^2) = 1.16$  eV. As a result, PBE+JJ nearly reproduces the exact reaction energy, whereas PBE gives >2 eV error (Table 7.9).

Method	Reaction	
	energy, eV	
PBE	0.44	
PBE+JJ	2.76	
Exact	2.79	

Table 7.9. Hydrogen cation dissociation energies

Having demonstrated the remarkable success of the DFT+JJ method for free atoms, next we will discuss the method's performance for molecules and introduce a methodology, aimed at eliminating atomic static correlation from DFT+JJ, in order to obtain accurate atomization and ionization energies.

### 7.4.6 Static Correlation Error-free DFT+JJ

The DFT+JJ expression (7.39) is inadequate for the task of predicting accurate reaction energies. To see this, let's consider the  $H_2 \rightarrow 2H$  reaction. We denote *s*orbital spin-up and spin-down occupancies as  $(o_{\uparrow}, o_{\downarrow})$ . The occupancies are (1,0) for spin-polarized free H atoms and (0.5,0.5) for each H atom in a singlet H<sub>2</sub>. Due to fractional orbital occupancies in H<sub>2</sub>, the JJ term will be positive; it will destabilize H<sub>2</sub> by whopping 4.64 eV, akin to the  $H_2^+$  case, discussed in the previous section. However, the PBE H<sub>2</sub> atomization energy error is only 0.17 eV.<sup>14</sup> Therefore, the DFT+JJ expression (7.39) will yield disastrous results in total disagreement with the experiment.

The JJ term is erroneously overestimated in (0.5,0.5) in comparison with (1,0). Ideally, JJ should be zero for both (0.5,0.5) and (1,0), since uncorrected PBE performs well. One may immediately recognize that the (0.5,0.5) energy overestimation problem is identical to that of the static correlation (SC) in atoms (see

Figure 6.3). DFT+JJ inherits the static correlation error (SCE) problem from global hybrids (Section 6.5.4.2). Therefore, by eliminating SCE in a reference free atom, we expect to obtain accurate reaction energetics with DFT+JJ.

Let's assume there are two degenerate and orthonormal one-electron solutions to Kohn-Sham equations for a given system, denoted as  $|1\rangle$  and  $|2\rangle$ . Consequently, there are two degenerate and orthonormal many-electron wave functions – Slater determinants  $\Psi_1 = |...1\rangle$  and  $\Psi_2 = |...2\rangle$ . Their identical energies are  $E_1 = \langle \Psi_1 | H_{eff} | \Psi_1 \rangle$  and  $E_2 = \langle \Psi_2 | H_{eff} | \Psi_2 \rangle$ . Any linear combination  $\Phi = c_1 \Psi_1 + c_2 \Psi_2$  is also a many-electron eigenstate with the identical energy  $E = \frac{\langle \Phi | H_{eff} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$  ( $E = E_1 = E_2$ ). The probability of finding an electron in the state  $|i\rangle$  (i.e., an average orbital

occupancy) is

$$o_i = |\langle i | \Phi \rangle|^2 = c_i^2 \tag{7.63}$$

We expand the state  $\Phi$  energy by taking advantage of the orthonormality of  $\Psi_1$ and  $\Psi_2$  states and the fact that the  $H_{eff}$  operator matrix is diagonal in the  $\Psi_1$ ,  $\Psi_2$  basis:

$$E = \frac{c_1^2}{c_1^2 + c_2^2} E_1 + \frac{c_2^2}{c_1^2 + c_2^2} E_2$$
(7.64)

Each of  $\Psi_1$  and  $\Psi_2$  determinants give rise to the corresponding kinetic, electrostatic, and exchange energy contributions. Therefore, the self-exchange energy in the  $\Phi$  state is

$$E_{se} = \frac{c_1^2}{c_1^2 + c_2^2} E_{1,se} + \frac{c_2^2}{c_1^2 + c_2^2} E_{2,se}$$
(7.65)

We conclude that the self-exchange energy of a system in the state  $\Phi$  with fractional occupancies  $o_i$  is required to be a linear combination of self-exchange energies of corresponding degenerate states with integer orbital occupancies. It is evident that the nonlinear dependence of the JJ term on occupancies (7.39) is inconsistent with (7.65).

The DFT+JJ theory is based on the hybrid functional construction, which stems from the adiabatic connection theorem. The latter is, in turn, derived from the single-determinant Kohn-Sham theory (Section 6.5.4.2). Among the states  $\Psi_1$ ,  $\Psi_2$ , and  $\Phi$ , only the first two are represented by single determinants. Therefore, we argue that it is only legitimate to apply the JJ term to the former two, i.e., to correct  $E_{1,se}$  and  $E_{2,se}$  in (7.65). In the H<sub>2</sub> example above, this is equivalent to representing (0.5,0.5) as  $0.5 \times (1,0) + 0.5 \times (0,1)$  and applying JJ to (1,0) and (0,1). Since the JJ term is zero for integer occupancies, it will not affect both H and H<sub>2</sub> energies, and thus the H<sub>2</sub> dissociation energy will be accurately predicted, with no spurious underbinding.

Fractional occupancies in atomic orbitals arise from two scenarios: (1) electron delocalization among degenerate orbitals of the same shell, and (2) electron transfer between shells and/or between atoms. In semilocal, spin-polarized DFT, energies of fractionally occupied orbitals are overestimated in the former and underestimated in the latter. The JJ term corrects (2), whereas (1) is taken care of (7.65). However, the solutions to (1) and (2), proposed above, are incompatible, since the expression (7.65) allows the JJ term to be applied only to orbitals with integer occupancies, for which it is trivially zero. Therefore, it is important to generalize (7.65) to the case of degenerate states containing a fractional, as opposed to integer, number of electrons.

The JJ term arises as a self-interaction correction in a fictitious free atom with orbital density matrix identical to that of a real system. Let's assume that the atom contains two degenerate orbitals  $|1\rangle$  and  $|2\rangle$ . We denote its total energy as  $E_{at}[\rho_a(o_1, o_2)]$ , where  $\rho_a$  is the atomic density, defined as  $o_1|\langle 1|1\rangle|^2 + o_2|\langle 2|2\rangle|^2$ , and  $o_i$  are occupancies of fixed degenerate orbitals. We rewrite the atomic density in the following form:

$$\rho_a(o_1', o_2') = f_1 \rho_a(o_1' - \delta, o_2' + \delta) + (1 - f_1) \rho_a(o_2' + \delta, o_1' - \delta)$$
(7.66)

Here  $o_i'$  are current orbital occupancies,  $0 \le o_i' \pm \delta \le 1$ , and  $f_1$  is defined by

$$f_1 = \frac{o_1' - o_2' - \delta}{o_1' - o_2' - 2\delta}$$
(7.67)

to preserve orbital occupancies in the left-hand and the right-hand parts of (7.66). Since the atomic orbitals are degenerate, the following equality holds:

$$E_{at}[\rho_a(o_1' - \delta, o_2' + \delta)] = E_{at}[\rho_a(o_2' + \delta, o_1' - \delta)]$$
(7.68)

For an exact density functional, energies of degenerate many-electron states and their linear superposition should be identical:<sup>1</sup>

$$E_{at}[\rho_a(o_1', o_2')] = f_1 E_{at}[\rho_a(o_1' - \delta, o_2' + \delta)] + (1 - f_1) E_{at}[\rho_a(o_2' + \delta, o_1' - \delta)]$$
(7.69)

To eliminate the SCE, we enforce this equality in analogy with (7.65). (7.69) eliminates SCE in the atomic limit: for example, if  $o'_1 = 0.75$ ,  $o'_2 = 0.25$ , and  $\delta = -0.25$ , then  $E_{at}[\rho_a(0.75, 0.25)] = 0.75E_{at}[\rho_a(1,0)] + 0.25E_{at}[\rho_a(0,1)] = E_{at,1D}[\rho_a(1,0)]$ , as it should be.

By analogy with the wave mechanics formalism (7.65), (7.69) implies the similar expression for self-exchange energies. The following modified DFT+JJ form results:

$$E_{JJ}[\rho_{a}(o_{1}', o_{2}')]$$

$$= f_{1}J[(o_{1}' - \delta)^{4/3} - (o_{1}' - \delta)^{2} + (o_{2}' + \delta)^{4/3} - (o_{2}' + \delta)^{2}]$$

$$+ (1 - f_{1})J[(o_{1}' - \delta)^{4/3} - (o_{1}' - \delta)^{2} + (o_{2}' + \delta)^{4/3} - (o_{2}' + \delta)^{2}]$$

$$- (o_{2}' + \delta)^{2}]$$

$$(7.70)$$

Or  

$$E_{JJ}[\rho_a(o_1', o_2')] = J[(o_1' - \delta)^{4/3} - (o_1' - \delta)^2 + (o_2' + \delta)^{4/3} - (o_2' + \delta)^2]$$
(7.71)

It is evident that the density matrix of the reference free atom is invariant to variations in the  $\delta$  parameter; i.e., any value  $\delta$  is consistent with the electron density distribution in a real system. The DFT variational principle requires the total energy to be



Figure 7.9. The JJ term as a function of  $\delta$  for various orbital occupancies.

minimized with respect to  $\delta$  in the ground state, with  $\max(1 - o'_1, o_2') - 1 \le \delta \le \min(o'_1, 1 - o_2')$  to ensure that orbital occupancies lie in the range [0,1]. Evidently, the  $E_{JJ}$  term is to be minimized with respect to  $\delta$ . In Figure 7.9 we plot  $E_{JJ}(\delta)$  for several combinations  $(o_1', o_2')$ , setting J = 1. It is clear that the minimal  $E_{JJ}$  value is degenerate and is reached for limiting  $\delta$  values  $\max(1 - o'_1, o'_2) - 1$  and  $\min(o'_1, 1 - o'_1, o'_2) = 1$ .

 $o_2'$ ). In other words,  $E_{JJ}$  is minimal when at least one of  $(o_i' \pm \delta)$  values is either 0 or 1. Since the resulting states are formed after "sliding down" the potential energy elevation to either of the ends, we informally refer to such states as "roller-coaster" states (RC states).

The discussion above generalizes (7.65) to fractional occupancies of degenerate states. As an example, the (0.9,0.4) state is represented as  $\frac{6}{7}(1.0,0.3) + \frac{1}{7}(0.3,1.0)$ . Then the JJ term can be applied to the RC states (1.0,0.3) and (0.3,1.0). Since JJ is zero for 1.0 occupancy, only the fractional part of  $(o'_1 + o'_2)$  is energetically important. Following the common convention, we denote the fractional part as  $\{o'_1 + o'_2\}$ .

The coefficients  $\frac{6}{7}$  and  $\frac{1}{7}$ , which we refer to as RC coefficients, are obtained from (7.67). This expression does not apply to systems with >2 degenerate orbitals. Below we introduce a more general procedure, using a 3-degenerate system as an example. Let's assume that the reference free atom has occupancies (0.3,0.4, 0.5). The RC states are (1,0.2, 0), (0,1, 0.2), and (0.2,0, 1). Their coefficients  $f_1$ ,  $f_2$ , and  $f_3$  can be obtained by solving a system of linear equations:

$$\begin{bmatrix} 0.3\\ 0.4\\ 0.5 \end{bmatrix} = \begin{bmatrix} 1 & 0.2 & 0\\ 0 & 1 & 0.2\\ 0.2 & 0 & 1 \end{bmatrix} \begin{bmatrix} f_1\\ f_2\\ f_3 \end{bmatrix}$$
(7.72)

The expression (7.71) for the RC states is the following:

$$E_{JJ}[\rho_a] = \sum_{\mu \ (atoms)} J_{\mu} \left[ \{o_1 + o_2\}_{\mu}^{4/3} - \{o_1 + o_2\}_{\mu}^2 \right]$$
(7.73)

In atoms, there are two types of degeneracy, associated with spin  $\sigma$  and magnetic quantum numbers  $m_L$ , respectively. Generalizing (7.73) to multiple degeneracies, we obtain

$$E_{xc}[\rho] = E_{xc}^{sl}[\rho] + \sum_{a=1}^{N_a} \sum_{L=0}^{L_a} J_{a,L} \left[ \left\{ \sum_{\sigma=1}^2 \sum_{m=1}^{2L+1} o_{a,L,m,\sigma} \right\}^{4/3} - \left\{ \sum_{\sigma=1}^2 \sum_{m=1}^{2L+1} o_{a,L,m,\sigma} \right\}^2 \right]$$
(7.74)

Here  $N_a$  is the total number of atoms, and  $L_a$  is the highest angular momentum number of atom *a*.

To derive the JJ contribution to the Kohn-Sham potential, we rewrite (7.74) in terms of RC states' orbital occupancies  $o'_i$  and RC coefficients  $f_i$ :

$$E_{xc}[\rho] = E_{xc}^{sl}[\rho] + \sum_{a=1}^{N_a} \sum_{L=0}^{L_a} J_{a,L} \sum_{s=0}^{2(2L+1)} f_{a,L,s} \sum_{m=0}^{2L+1} \sum_{\sigma=1}^{2} \left( o_{a,L,s,m,\sigma}^{\prime 4/3} - o_{a,L,s,m,\sigma}^{\prime 2} \right)$$
(7.75)

Within a projection sphere, the matrix elements of the one-electron XC potential (spin-polarized case with spin-up/spin-down densities  $\rho^1, \rho^2$ ) are the following:<sup>212</sup>

$$V_{jl}^{\sigma} = \frac{\delta E_{xc}[\rho^1, \rho^2]}{\delta \rho_{lj}^{\sigma}} = \frac{\delta E_{xc}^{sl}}{\delta \rho_{lj}^{\sigma}} + \frac{\delta E_{JJ}}{\delta \rho_{lj}^{\sigma}}$$
(7.76)

To derive the last term in (7.76), first we note that in a rotationally invariant theory, occupancies  $o_i$  in (7.74) are eigenvalues of the reference atom density matrix  $\rho$ . The derivative of  $o_i$  with respect to the density matrix element  $\rho_{jk}$  is  $(w_i \otimes w_i^T)_{jk}$ , where  $w_i$  is the density matrix eigenvector, corresponding to the eigenvalue  $o_i$ . Without the SCE elimination procedure, (7.76) would be

$$V_{jl}^{\sigma} = \frac{\delta E_{xc}^{sl}}{\delta \rho_{lj}^{\sigma}} + \sum_{a=1}^{N_a} \sum_{L=0}^{L_a} J_{a,L} \sum_{m=0}^{2L+1} \sum_{\sigma=1}^{2} \left( w_{a,L,m,\sigma} \otimes w_{a,L,m,\sigma}^{\mathrm{T}} \right)_{lj} \times \left( \frac{4}{3} o_{a,L,m,\sigma}^{1/3} - 2 o_{a,L,m,\sigma} \right)$$
(7.77)

After the SCE elimination is introduced, (7.77) becomes

$$V_{jl}^{\sigma} = \frac{\delta E_{xc}^{sl}}{\delta \rho_{lj}^{\sigma}} + \sum_{a=1}^{N_a} \sum_{\substack{L=0\\2(2L+1)}}^{L_a} J_{a,L} \sum_{m=0}^{2L+1} \sum_{\sigma=1}^{2} \left( w_{a,L,m,\sigma} \otimes w_{a,L,m,\sigma}^{\mathrm{T}} \right)_{lj} \times \sum_{s=0}^{2(2L+1)} f_{a,L,s} \left( \frac{4}{3} o'_{a,L,m,\sigma,s}^{1/3} - 2o'_{a,L,m,\sigma,s} \right)$$
(7.78)

Preliminary tests of (7.78) revealed convergence difficulties, when  $f_{a,L,s}$ 's are calculated from (7.72). An alternative is to define  $f_{a,L,m,\sigma} = \frac{o_{a,L,m,\sigma}}{\sum o_{a,L,m,\sigma}}$ . Tests for the new definition of weighting factors are underway.

Having introduced the SCE-free DFT+JJ scheme, we will test it on simple molecules of monovalent elements next.

### 7.4.7 Homolytic Molecules

To evaluate the method, we performed ionization energy (IE) calculations for the following molecules: H<sub>2</sub>, Li<sub>2</sub>, Li<sub>3</sub>, Li<sub>4</sub>, Na<sub>2</sub>, K<sub>2</sub>, Rb<sub>2</sub>, Cs<sub>2</sub>, Cu<sub>2</sub>. An interesting fact is that *J* values, previously employed for atoms, yield only satisfactory results for molecules – the JJ term overcorrects IE. This is expected in relation to the projection radius choice for s-elements – their projection spheres overlap, and thus the atomic basis set is not complete. Therefore, a different set of *J* values must be chosen that would take into account electron density reoptimization outside the PAW augmentation sphere.

To obtain new parameters, we begin with fully relaxed, spin-polarized atoms. We made an observation that, if we apply our theorem to eigenvalues of fully relaxed atoms, the resulting self-exchange energies of hypothetical Z-representable states are lower than those in the frozen atoms, suggesting that they correspond to more diffuse densities. We hypothesized that such densities will be relevant to homolytic molecules and decided to try new *J* values for IE calculations. The results are reported in Figure 7.10. Similar to atoms, PBE underestimates IE by as much as 5 eV (H<sub>2</sub> molecule). Remarkably, PBE+JJ yields nearly chemical accuracy with the largest error of only -0.15 eV (Li<sub>2</sub>)! The mean absolute error for 9 molecules is only 0.09 eV. It is truly remarkable that the *J* value, calculated for a relaxed free atom, is capable of producing nearly exact IE in molecules. The exact reason of this phenomenon is unknown; we speculate that spin polarization and nearby nuclei have a similar contracting effect on the electron density, "locking" significant part of it inside the augmentation sphere. As



Figure 7.10. Comparison of experimental ionization energies with predicted ones using PBE and PBE+JJ methods.

a result, electron density variations are quite limited, and the J value is transferable between atoms and molecules. Additional studies are required to shed light on this effect.

### 7.5 Conclusions and Outlook

We have discovered the DFT+JJ method that holds promise to bring the accuracy of *ab initio* predictions to another level at low extra computational cost. The method appears to completely eliminate the many-electron self-interaction error, as manifested by near-chemical-accuracy predictions of ionization energies, H<sub>2</sub><sup>+</sup> dissociation energy, and metal oxide lattice constants, as well as accurate predictions of oxide cohesive and molecular atomization energies. We derived DFT+JJ equations by introducing several novel concepts, such as regional hybrids, Z-representable densities, correlated LDA/GGA, a theorem relating self-exchange with atomic eigenvalues, and elimination of the static correlation error from the JJ part. In the future, it is desirable to perform extensive method benchmarking and extend the formalism to atomic states of p and d symmetry. The method demonstrates the power and utility of remarkably simple, yet nonempirical models, capable of making nearly exact predictions of properties of chemical interest. Inspired by DFT+JJ, we have made initial progress in developing simple and transparent models to address two other semilocal functional flaws - static and dynamic correlation, which are the subject of future publications.

### Chapter 8

### SUMMARY AND OUTLOOK

#### 8.1 Dissertation Conclusions

This thesis reported scientific advancements in two related areas: catalysis and quantum chemistry. In catalysis, the radical-mediated C-O bond activation mechanism was discovered, and its generality was established for various substrates with certain double bond arrangements, reducible metal oxide catalysts, and surface oxide-covered bimetallics. In quantum chemistry, a new method was proposed to increase the accuracy of computational predictions of chemical properties.

Chapter 2 reported fundamentals of interactions of substituted furans with metallic catalyst surfaces in the presence of a strongly adsorbing solvent (toluene). The observed H/D exchange rate trend on an oxophilic catalyst (Ru) was explained by the interplay of an oxygen content in a substrate, affecting its binding energy, and its bulkiness, causing steric interactions with abundant co-adsorbed toluene solvent molecules.

Chapter 3 reported the trifunctional mechanism of the catalytic transfer hydrogenation of furfural on the Ru/RuO<sub>2</sub> catalyst in a 2-propanol solvent. Lewis acid sites catalyzed direct intermolecular hydride transfer from 2-propanol to furfural to form furfuryl alcohol; oxygen vacancies activated the C-O bond in the latter via the resonance-stabilized radical; and metal sites dehydrogenated 2-propanol and produced H<sub>2</sub>, which was crucial for vacancy formation on RuO<sub>2</sub>. The constructed microkinetic models reproduced experimental data in both a liquid environment and ultrahigh vacuum, thus bridging the pressure gap.

Chapter 4 extended the conjugation-driven C-O bond activation mechanism to other reducible oxides and substrates with double bonds in  $\alpha$ -position to the C-O bond. In addition to observed generalities in catalysis by metal oxides, the chapter also reported unexpected diversity in vacancy formation mechanisms and surface terminations in a reducing environment. Chapter 4 also developed a novel procedure aimed at eliminating referencing errors in microkinetic models on metal oxides.

Chapter 5 extended the radical C-O bond activation mechanism to bimetallic nanoparticles, covered with an oxide monolayer. A mean-field-type structural model of a catalyst was developed. The proposed metallic core-oxide shell structure, containing cobalt oxide with an unusual  $Co_3O_2$  stoichiometry, was consistent with all experimental data.

Chapter 6 and Chapter 7 introduced the DFT+JJ method, which corrected selfinteraction error in atomic reference systems, enabling accurate predictions of atomic and molecular ionization energies, molecular atomization energies, as well as oxide cohesive energies and lattice constants. Chapter 7 also developed a novel procedure to eliminate static correlation error in the JJ term.

# **8.2 Future Directions**

#### 8.2.1 Quantum Chemistry

The DFT+JJ method yielded promising results; however, it is still unclear why certain aspects of the method work the way they do. To this end, the following fundamental questions are to be addressed: (1) Does DFT+JJ work only in conjunction

with the PAW formalism, or is it basis set independent? Can it be implemented in codes that employ gaussian basis sets (Gaussian software)? (2) What is the physical basis of various ways to extract the J parameter from atomic eigenvalues? (3) Can the Z-representability requirement be derived mathematically? Addressing these questions will greatly benefit from the fact that the most interesting features of DFT+JJ are already present in the simplest quantum mechanical systems (H and H<sub>2</sub>), for which analytical solutions of approximate Kohn-Sham equations are probably available.

The JJ correction scheme can be integrated with the next-generation meta-GGA functionals, such as TPSS<sup>292</sup>, revTPSS<sup>296</sup>, and a promising SCAN<sup>373</sup>, bringing even greater predictive accuracy to computational catalysis and chemistry. The logical next step toward "exact DFT" will entail methods for modeling van der Waals interactions, such as D3/D4<sup>235,374</sup> or Tkachenko-Scheffler<sup>375</sup>, enabling accurate treatment of an even wider range of systems, including those with mixed covalent and weak interactions. Also, the possibility of adding interatomic (in addition to intraatomic) JJ terms should be considered, in order to describe four-electron interatomic interactions correctly (lone pair-lone pair, closed shell-closed shell), which are known to be poorly modeled by GGA<sup>376</sup>.

Successful correction of the self-interaction error by DFT+JJ brings about a natural follow-up question – can similar orbital occupancy-based expressions be developed to address static and dynamic correlation errors as well? If this is so, then all DFT errors will essentially be eliminated.

For broader impact in catalysis and chemistry communities, DFT+JJ should, in addition to its original implementation in VASP<sup>45</sup>, be implemented in major U.S. and

European DFT codes, such as Quantum Espresso<sup>377</sup>, GPAW<sup>378</sup>, Qbox, FHI-aims<sup>379</sup>, and CP2K<sup>380</sup>.

#### 8.2.2 Catalysis

In Section C.4 we demonstrated the capability of an appropriately referenced microkinetic model to describe regularities of C-O bond activation on the TiO<sub>2</sub> catalyst. The next step is to extend this approach to other materials and take advantage of high-quality experimental data, reported in Figure 4.2. Furfuryl alcohol deoxygenation to 2-methyl furan represents a convenient reaction system to benchmark various DFT methods, such as DFT+JJ.

The most active C-O bond activation catalysts (RuO<sub>2</sub> and IrO<sub>2</sub>) are (1) expensive and (2) unstable in the reducing environment. More sophisticated catalyst architectures hold promise to address these drawbacks. For example, modifying less expensive and less active oxides (e.g., TiO<sub>2</sub>) with doping or supporting single metal atoms is known to increase oxide reducibility, and thus can provide a means to create more reducible surface sites, embedded into the less reducible framework, which will maintain its integrity in the reducing environment, rendering the catalyst more stable.

Finally, there is an opportunity to conduct efficient hydrodeoxygenation on inexpensive catalysts via photocatalysis. Excitation of valence band electrons by UV-vis radiation creates surface vacancies at room temperature, which can pull the oxygen out of biomass-derived molecules. Such a photocatalytic process may find future applications in the context of  $CO_2$  conversion to fuels and chemicals via oxygenate intermediates, driven by sunlight.

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#### Appendix A

# RING ACTIVATION OF FURANIC COMPOUNDS ON RU-BASED CATALYSTS

#### A.1 Parameterization of Microkinetic Modeling

Thermochemical parameters of gaseous species were taken either from the Burcat database<sup>381</sup> (except for 2-MF that were taken from Ref. <sup>382</sup>) or from high-accuracy Gaussian calculations<sup>383</sup>. A combination of the COSMO-SAC method<sup>384</sup> and the Peng-Robinson equation of state, as implemented in ASPEN PLUS V8.2, was employed to obtain Gibbs free energies of pure components and their activity coefficients in the mixture at 300 psig and 140 °C. The molar density of the bulk phase was set to the one computed at experimental conditions using ASPEN.

Two types of Ru surface sites were considered: on one site, competitive adsorption of carbon-containing species occurred, and on the other, atomic hydrogen and deuterium adsorb only (due to its small size, H can adsorb on sites not accessible to bulkier species). The density of Ru sites of the first type was taken to be 22 µmol per 0.1 g of the catalyst, consistent with CO chemisorption data<sup>175</sup>. Chemical potentials of surface species were estimated using statistical mechanics with DFT results at 0 K and vibrational frequencies<sup>385</sup>. We assume that all translational and rotational degrees of freedom of surface species are converted into vibrational degrees of freedom. Deuterium-substituted species were taken to have the same thermodynamic properties as their conventional counterparts. Adsorption enthalpies of

surface species were corrected for thermodynamic consistency<sup>386</sup>. Pure gaseous toluene, IPA, and 2-MF were chosen as thermodynamic references. Sticking coefficients for toluene, furan compounds, and IPA on a free Ru surface were taken to be equal to  $10^{-7}$ , in the middle of the sticking coefficient range of  $10^{-6}$ – $10^{-8}$  reported for alkylthiol adsorption from ethanol solution on gold <sup>387</sup>. In general, the model results are insensitive to the specific sticking coefficient values.

We determined that the site occupancy on the p(6x4) Ru(0001) slab is 6 for toluene, 4 for IPA, furan, and 3-MF, and 5 for furfuryl alcohol. These numbers agree well with experimental data for similar size molecules: benzene and cyclopentene on Pt(111) have site occupancies of 6 and 4, respectively<sup>388</sup>. Site occupation numbers of exchange intermediates were taken to be the same as those of their parent compounds.

The elementary reaction rates were calculated using transition state theory. Gibbs free energies of activation were approximated with 0 K DFT reaction barriers. ZPE and temperature corrections, calculated for selected Gibbs reaction barriers, did not exceed 0.1-0.2 eV and did not affect reaction rate trends. Activation barriers for the dehydrogenation of IPA to acetone were calculated in the presence of co-adsorbed toluene and are reported in Table A.1. For local sensitivity analysis (SA), the degree of rate control was calculated via perturbations of kinetic parameters for each elementary step <sup>65,389,390</sup>. Reaction path analysis (RPA) has been performed as described elsewhere <sup>391</sup>.

Lateral interactions within the adlayer were accounted for using a twoparameter linear model<sup>392</sup> with minimum threshold coverages and slopes determined from DFT calculations. Adsorption energies were calculated at two toluene coverages (0.38 and 0.75 ML; Figure A.1; the latter were done on a 6x4 unit cell). Lateral interactions experienced by 2-MF and 3-MF intermediates were taken to be equal. Slopes for species self-interactions (H-H, toluene-toluene) were multiplied by two to obtain correct differential adsorption enthalpies.<sup>392</sup>



Figure A.1. Binding energies of exchange intermediates as a function of toluene coverage: adsorbed furans (a) and products formed after ring-opening (b) and subsequent dehydrogenation (c). Gas phase reactants and H on separate slabs are used as a reference. 3-MF:  $R_1$ =H,  $R_2$ =CH<sub>3</sub>; furan:  $R_1$ =H,  $R_2$ =H; furfuryl alcohol:  $R_1$ =CH<sub>2</sub>OH,  $R_2$ =H.



Figure A.2. Structures of 2-MF (a) and 2-MF/D adduct (b) on the Ru(0001) surface. Light grey - hydrogen; dark grey - carbon; red - oxygen; green - deuterium.



Figure A.3. Ring-opening possibilities in 2-MF. Reaction barriers (reaction energies) are reported in eV.



Figure A.4. Structures of IS, TS, and FS of the ring-opening step in 2-MF, 3-MF, furan, and FA in mechanism 6.

Reaction step	Reaction barrier (reaction energy), eV
$\begin{array}{c} \text{CH}_3\text{-}\text{CH}(\text{OH})\text{-}\text{CH}_3 \not\rightarrow \text{CH}_3\text{-}\\ \text{CH}(\text{O})\text{-}\text{CH}_3 + \text{H} \end{array}$	0.8 (-0.5)
$CH_3-CH(O)-CH_3 \rightarrow CH_3-C(O)-CH_3+H$	0.8 (+0.2)
$CH_3-CH(OH)-CH_3 \rightarrow CH_3-C(OH)-CH_3 + H$	1.7 (+1.1)
$CH_3-C(OH)-CH_3 \rightarrow CH_3-C(O)-CH_3+H$	0.4 (-0.2)

Table A.1. Reaction barriers (energies) for isopropanol (IPA) dehydrogenation to acetone in the presence of 0.75 ML co-adsorbed toluene.

Table A.2. Reaction barriers (energies) for ring-opening (RO) and subsequent dehydrogenation steps.

Reactant	RO of C <sub>2</sub> -O	$C_5-H \rightarrow C_5 + H$	RO of C <sub>5</sub> -O	$C_5-H \rightarrow C_5 + H$
2-MF	0.55 (-0.5)	1.04 (-0.36)	0.62 (-0.91)	0.20 (-0.44)
3-MF	0.64 (-0.81)	-	0.62 (-0.91)	0.19 (-0.43)
Furan	0.54 (-0.92)	-	0.54 (-0.92)	0.19 (-0.44)
FA	0.38 (-0.42)	0.31 (-0.22)	0.75 (-0.84)	0.17 (-0.48)

Table A.3.	Binding	energies	of	various	com	pounds	on	Ru(	0001	).
	()	()								

Compound	Binding energy, eV			
	low coverage limit	with 0.75 ML co-		
		adsorbed toluene		
2-MF	-1.93	-		
3-MF	-1.96	-0.71		
Furan	-1.86	-0.96		
FA	-2.42	-1.43		
Furfural	-2.49	-		
Toluene	-2.57	-0.65*		

\*Toluene desorption at 1 ML coverage.

#### Appendix B

# CONJUGATION-DRIVEN "REVERSE MARS-VAN KREVELEN"-TYPE RADICAL MECHANISM FOR LOW TEMPERATURE C-O BOND ACTIVATION

#### **B.1** Details of the DFT Setup; Benchmarking of Vacancy Formation Energetics.

Core electrons were modeled as projector-augmented waves<sup>47,48</sup>; valence electrons were treated in a plane wave basis set with a kinetic energy cutoff of 400 eV. During electronic energy optimization, the initial Hamiltonian was obtained using a superposition of atomic charge densities and was fixed during the first 10 electronic iterations. The Davidson algorithm was used for initial non-self-consistent steps. Subsequent electronic optimizations were carried out using the RMM-DIIS algorithm with the electronic density updated by means of the Pulay's mixing scheme, using default parameters as implemented in VASP. Electronic relaxations were carried out until the energy difference between two sequential electronic iterations was smaller than  $10^{-4}$  eV. All structures have been optimized to the force convergence threshold of 0.05 eV/Å.

For Ru(0001), we used the Monkhorst-Pack  $3 \times 3 \times 1$  k-point grid to sample the first Brillouin zone. For RuO<sub>2</sub>(110), the first Brillouin zone was sampled at the  $\Gamma$ -point, as a compromise between accuracy and computational cost. All calculations on the RuO<sub>2</sub>(110) surface were spin-polarized. For Ru(0001), spin polarization was turned off, as it had a negligible effect on energetics.

We employed a finite difference approach to calculate the Hessian matrix and vibrational frequencies. All surface species were assumed to possess only vibrational degrees of freedom.

A combination of nudged elastic band (NEB), climbing-image NEB (10 images between initial and final states), and dimer methods<sup>57-61</sup> was used in calculations of reaction barriers.  $10^{-5}$  eV electronic energy threshold was employed for the dimer method. Forces were converged until 0.1 eV/Å. Transition states were confirmed by vibrational analysis.

Performance of exchange-correlation functionals for processes involving oxides and oxygen vacancies is typically evaluated against thermodynamic literature data for bulk phase reactions<sup>349,393</sup>. In order to estimate how accurate PBE-D3 is in describing vacancy formation energetics, we calculated the enthalpy of the following reaction:

$$RuO_2$$
 (bulk) +  $2H_2 = Ru$  (bulk) +  $2H_2O$  (gas)

Gas-phase calculations for H<sub>2</sub>O and H<sub>2</sub> were carried out at a single  $\Gamma$  point in the 20 × 21× 22 Å supercell. Vibrational contributions to the enthalpy were calculated from DFT; the  $\frac{5}{2} \times RT$  (or  $\frac{6}{2} \times RT$ ) term, due to translational and rotational degrees of freedom, and the PV term were included for gas species. The phonon contribution to the bulk energies was estimated within the Einstein crystal model with characteristic frequencies of 25 meV for Ru and 80 meV for O atoms<sup>394</sup>. The reaction energy was found to be -1.50 eV (-1.53 eV without D3 correction). The difference with the experimental value of -1.76 eV<sup>395</sup> conforms to the typical accuracy of the DFT method (~0.2 eV). The reaction energy error per oxygen atom is 0.13 eV, providing an orderof-magnitude estimate for the error in vacancy formation energy. The agreement between experimental and simulated  $RuO_2(110)$  surface reduction kinetics (see Section S3) further confirms the accuracy of the DFT setup.



Figure B.1. Furfural hydrogenolysis mechanisms. a) Horiuti-Polanyi-type sequential hydrogenation on Ru(0001); b) Meerwein-Ponndorf-Verley (MPV) interhydride transfer on Lewis acid sites of  $RuO_2(110)$ <sup>4</sup>. Reaction barriers (reaction energies) are given in eV.

Reaction	#	DFT reaction energy, eV	DFT reaction barrier, eV				
Furfural hydrogenation to furfuryl alcohol							
FCHO + * = FCHO*	-	-2.54	N/A				
$0.5 H_2 + * = H*$	-	-0.72	N/A				
$FCHO^* + H^* = FCH_2O^* + *$	1	+0.33	0.78				
FCHO* + H* = FCHOH* + *	2	+0.54	1.28				
$FCH_2O^* + H^* = FCH_2OH^* + *$	3	+0.36	0.95				
$FCHOH* + H* = FCH_2OH* + *$	4	+0.13	1.56				
$FCH_2OH + * = FCH_2OH*$	-	-2.50	N/A				
Furfuryl alcohol conversion to 2-methyl furan							
$FCH_2OH^* + * = FCH_2^* + OH^*$	5	-0.84	0.91				
$FCH_2O^* + * = FCH_2^* + O^*$	6	-1.27	0.68				
$FCH_2^* + H^* = FCH_3^*$	7	+0.46	0.92				
$FCH_3^* = FCH_3 + *$	-	+1.97	N/A				
	O ren	noval					
$O^* + H^* = OH^* + *$	8	+0.76	1.63				
$OH^* + H^* = H_2O^*$	9	+0.52	1.29				
$H_2O^* = H_2O + *$	-	+0.66	N/A				
C-O scission in fu	rfuryl alco	ohol on 0.25ML O/Ru(	0001)				
FCH <sub>2</sub> OH** = FCH <sub>2</sub> -OH**	10	+1.24	N/A				
$FCH_2O^{**} = FCH_2 - O^{**}$	11	+1.42	N/A				

Table B.1. DFT reaction energies and barriers on a Ru(0001) surface. Index numbers correspond to structures in Figure B.1. For bimolecular reactions, energies are reported with respect to species adsorbed on separate slabs.

Notation:

\* - intact Ru(0001) surface;

\*\* - Ru(0001) with pre-adsorbed 0.25 ML O;

F-furfuryl fragment C<sub>4</sub>H<sub>3</sub>;

FCHO – furfural;

FCH<sub>2</sub>OH – furfuryl alcohol;

FCH<sub>3</sub>-2-methyl furan;

 $FCH_2-O(H)^{**} - O(OH)$  species on a O-precovered surface with a physisorbed

furfuryl radical FCH<sub>2</sub> nearby

N/A – a reaction barrier was not calculated



Figure B.2. Optimized structures of initial, transition, and final states that correspond to reactions in Table B.1. Teal atoms - Ru, red atoms - oxygen, grey atoms - carbon. Two bottom Ru layers are not shown. The figure continues on the next page.



#### **B.2** Cooperativity Effects of Ru and RuO<sub>2</sub>.

Binding	Ru(0001)	$RuO_2$	$RuO_{2}(110)$	RuO <sub>2</sub> (110)-	RuO <sub>2</sub> (110)
energies,		(110)-	(hydroxylated)-	Vacancy	(hydroxylated)-
eV		Rucus	Ru <sub>cus</sub> <sup>1</sup>		Vacancy <sup>2</sup>
0	-0.47	+0.80	+0.78	+0.43	+0.12
OH	-0.44	-0.38	-0.63	-1.12	-0.79
$H_2O$	-0.65	-1.70	-1.18	-0.59	-0.61

Table B.2. OH<sub>x</sub> binding energies (DFT) with respect to H<sub>2</sub>O and H<sub>2</sub> in vacuum.

 $^{1}(3x2)$  surface supercell involves 6 O<sub>br</sub> atoms capped with H.

 $^{2}(3x2)$  surface supercell involves 5  $O_{br}$  atoms capped with H atoms, and 1 oxygen vacancy.

We studied cooperativity effects of Ru and RuO<sub>2</sub> in contact with each other by constructing a model system, consisting of a  $p(6\times2)$  RuO<sub>2</sub>(110) supercell with two O-Ru-O trilayers (top two atomic layers were relaxed). Ru<sub>7</sub> either in a form of a nanoparticle in its most stable configuration<sup>396</sup> or a one-atom-thick hexagonal nanocluster was attached to the surface. Two limiting cases of metal/metal-oxide interface atomic structure were considered: with and without an interfacial oxygen layer between Ru<sub>7</sub> and RuO<sub>2</sub> (referred to as RuO<sub>2</sub>(110)<sub>ox</sub> and (RuO<sub>2</sub>(110)<sub>red</sub>, respectively). We calculated adhesion energies as  $\Delta E_{ad} = E_{Ru/RuO2} - E_{RuO2} - E_{Ru(NP)}$ , where  $E_{Ru/RuO2}$  is the energy of the combined metal/metal oxide structure,  $E_{RuO2}$  is the energy of the relaxed structure after removal of the metallic cluster, and  $E_{Ru(NP)}$  is the Ru<sub>7</sub> nanoparticle energy in vacuum (Table B.3). We found that the Ru<sub>7</sub> monolayer

island attached to  $RuO_2$  via the oxygen layer ( $RuO_2(110)_{ox}$ - $Ru_7(ML)$ ) is the most thermodynamically stable configuration. Formation of similar in shape, yet different in size, hexagonal islands have been observed in STM studies<sup>129</sup>.

Table B.3. Adhesion energies of a Ru7 nanoparticle (NP) or a monolayer (ML) on the RuO2(110) surface.

Structures	Ru <sub>7</sub> /RuO <sub>2</sub> (110)
	adhesion energies,
	eV
RuO <sub>2</sub> (110)red-Ru <sub>7</sub> (NP)	-8.6
RuO <sub>2</sub> (110)red-Ru <sub>7</sub> (ML)	-8.8
RuO <sub>2</sub> (110)ox-Ru <sub>7</sub> (NP)	-14.3
RuO <sub>2</sub> (110)ox-Ru <sub>7</sub> (ML)	-16.3

In order to assess the RuO<sub>2</sub> effect on the oxophilicity of the metallic Ru, we calculated oxygen binding energies on RuO<sub>2</sub>(110)red-Ru<sub>7</sub> (ML) and RuO<sub>2</sub>(110)ox-Ru<sub>7</sub> (ML). To minimize system size effects, we also calculated O binding energy on a Ru<sub>7</sub> island supported on a Ru(0001) slab as a reference (denoted as Ru(0001)-Ru<sub>7</sub>). The structures are displayed in Figure B.3(a-c); energetics is provided in Table B.4.

Table B.4. RuO2 effect on oxygen binding energies on Ru7.

Structures	Oxygen binding energy with respect to H <sub>2</sub> O and H <sub>2</sub> , eV
Ru(0001)-Ru7	-0.11
RuO2(110)ox-Ru7	-0.53
RuO <sub>2</sub> (110)red-Ru <sub>7</sub>	-0.73

The data suggest that the interaction of  $Ru_7$  with the  $RuO_2$  (110) substrate makes the metallic Ru more oxophilic. This is in agreement with electron-withdrawing effects of oxide supports on metal nanoparticles, which depopulate their antibonding states and increase species binding energies<sup>397</sup>.

In order to determine the ability of metallic Ru to modify C-O scission activity of Lewis acid sites of RuO<sub>2</sub>, we calculated O and OH binding energies on Ru<sub>cus</sub> sites of RuO<sub>2</sub>(110) in the presence or absence of a Ru<sub>7</sub> island attached nearby. Structures are given in Figure B.3(d,e); results are provided in Table B.5. Overall, metallic Ru has either a minor or detrimental effect on O and OH binding energies. Consequently, we expect no enhancement of C-O scission rates on Ru<sub>cus</sub> sites. Similarly, Ru has only a small effect on vacancy formation via H-O-H removal on a fully hydroxylated



Figure B.3. (a-c) oxygen binding to the  $Ru_7$  island; (d-e) Vacancy formation via H-O-H removal on  $RuO_2(110)$  in the presence or absence of the  $Ru_7$  island. In binding energy calculations, species to be removed (O or H<sub>2</sub>O) are circumscribed with black ovals.

surface.

Structures <sup>1</sup>	0	OH	$H_2O$
RuO <sub>2</sub> (110)	+0.93	-0.42	N/A
RuO <sub>2</sub> (110)red-	+0.94	-0.46	N/A
Ru <sub>7</sub>			
RuO <sub>2</sub> (110)ox-	+1.27	-0.03	N/A
Ru <sub>7</sub>			
RuO <sub>2</sub> (110)	N/A	-1.20	-0.77
(vacancy)			
RuO <sub>2</sub> (110)red-	N/A	-1.35	-1.07
Ru7 (vacancy)			
RuO <sub>2</sub> (110)ox-	N/A	-1.25	-1.24
Ru7 (vacancy)			

Table B.5. Effect of Ru on O, OH, and H<sub>2</sub>O binding energies on RuO<sub>2</sub>(110).

 ${}^{1}$ RuO<sub>2</sub>(110) oxide structure consists of two O-Ru-O trilayers in a (6x2) supercell; all O<sub>br</sub> surface atoms are capped with H. All binding energies are reported with respect to stoichiometric amounts of H<sub>2</sub> and H<sub>2</sub>O in vacuum.

Reaction	#	DFT reaction	DFT reaction			
		energy, eV	barrier, eV			
2-propanol dehydrogenation (pristine surface)						
$ACHOH + Ru_{cus} = ACHOH_{cus}$	-	-	N/A			
$ACHOH_{cus} + O_{br} = ACHO_{cus} - OH_{br}$	1	-0.18	0.07			
$ACHO_{cus}-OH_{br}+O_{br} = ACO_{cus}-2OH_{br}$	2	-1.07	0.49			
$ACO_{cus} = ACO + Ru_{cus}$	-	-1.83	N/A			
2-propanol dehydrogena	tion (hydr	oxylated surface)				
$ACHOH + Ru_{cus} = ACHOH_{cus}$	-	-1.29	N/A			
$ACHOH_{cus} + 2O_{br} = ACO_{cus} + 2OH_{br}$	3	+1.23	N/A			
$ACO_{cus} = ACO + Ru_{cus}$	-	-1.32	N/A			
Vacancy formation mechanisms prop	posed in the	he literature (pristi	ne surface)			
$2OH_{br} = V + H_2O^1$	4	+1.81	N/A			
$H_{cus} + OH_{br} = H_2O_{cus} + V^2$	5	+0.32	1.96 <sup>3</sup>			
Reactions with Obr (	hydroxyla	ated surface)				
$O_{br} + H_2 = H_2 O_{br}$	6	-0.68	$1.59^{4}$			
$H_2 + Ru_{cus} = H_{2,cus}$	-	-0.48	N/A			
$H_{2,cus} + O_{br} = H_{cus} + OH_{br}$	7	-0.64	0.54			
$H_{cus} + O_{br} = Ru_{cus} + OH_{br}$	8	-0.86	0.85			
Reactions with OH <sub>br</sub> (hydroxylated surface)						
$H_{cus} + OH_{br} = Ru_{cus} + H_2O_{br}$	9	+0.32	0.89			
$H_{2,cus} + OH_{br} = H_{cus} + H_2O_{br}$	10	+0.24	0.39			
H <sub>2</sub> O diffusion and desorp	tion (hyd	roxylated surface)				
$H_2O_{br} = V + H_2O$	-	+0.59	N/A			
$H_2O_{br} + Ru_{cus} = V - H_2O_{cus}$	11	-0.58	0.40			
$V-H_2O_{cus} = V + H_2O$	-	+1.18	N/A			
Furfuryl alcohol	C-O hydro	ogenolysis				
$FCH_2OH + Ru_{cus} = FCH_2OH_{cus}$	-	-1.58	N/A			
$FCH_2OH + V = FCH_2OH_{br}$	-	-0.76	N/A			
$FCH_2OH_{br} = FCH_2 - OH_{br}^5$	12	+0.11	0.26			
$FCH_2-OH_{br} = FCH_2-HO_{br}^6$	13	+0.16	0.30			
$FCH_2-HO_{br} = FCH_3-O_{br}$	14	-1.07	0.06			
$FCH_3-O_{br} = FCH_3 + O_{br}$	-	+0.40	N/A			
$FCH_2-OH_{br}+OH_{br}=(H@C3-FCH_2)-$	15	+0.01	0.07			
$OH_{br} + O_{br}^{7}$						
$FCH_2OH_{cus} + OH_{br} = FCH_2 - H_2O_{cus} - O_{br}^8$	16	+1.14	N/A			

Table B.6. DFT reaction energies and barriers on a RuO2(110) surface. Index numbers correspond to structures in Figure B.3.

<sup>1</sup>Recombination of two neighboring  $OH_{br}$  groups, as found on  $TiO_2(110)$  (see the main text for references); <sup>2</sup> $OH_{br}$  shift with concomitant  $H_2O_{cus}$  formation, as suggested for  $RuO_2(110)$ ; <sup>3</sup>No transition state is found; we could not get NEB forces <0.5 eV/Å; <sup>4</sup>direct adsorption of  $H_2$  on  $O_{br}$  is kinetically unfavorable; <sup>5</sup>C-O bond scission yields furfuryl radical FCH<sub>2</sub>, adsorbed next to  $OH_{br}$ ; <sup>6</sup> $OH_{br}$  rotation; <sup>7</sup>H addition to the furfuryl radical at C<sub>3</sub> position; <sup>8</sup>Brønsted-acid like mechanism.

Notation:

 $Ru_{cus}-coordinatively$  unsaturated surface Ru site

Obr-surface bridging oxygen atom

V-oxygen vacancy formed in place of  $O_{br}$ 

ACHOH - 2-propanol

ACO – acetone

FCH<sub>2</sub>OH – furfuryl alcohol

FCH<sub>2</sub> – furfuryl radical

FCH<sub>3</sub>-2-methyl furan

N/A - reaction barrier was not calculated



Figure B.4. Optimized structures of initial, transition, and final states that correspond to reactions in Table B.6. Teal atoms - Ru, red atoms - oxygen, grey atoms - carbon. The two bottom Ru layers are not shown. The figure continues on the next pages.

5)		N/A	
6)	<b>111</b>	uit, Mi	
7)			<b>***</b>
8)			
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Table B.7. Total Bader charge of a furfuryl alcohol molecule.

Structure	Total Bader charge	Charge transfer to the surface
FCH <sub>2</sub> OH (gas)	0.0002	-
$FCH_2OH - RuO_2$	0.0901	0.0899
(110) [Ru <sub>cus</sub> site]		
$FCH_2OH - RuO_2$	0.0892	0.0890
(110) [vacancy site]		

# **B.3** Microkinetic Model (MKM) of RuO<sub>2</sub>(110) Surface Reduction at Ultrahigh Vacuum (UHV) Conditions

In the MKM, two types of surface sites are considered:  $Ru_{cus}$  and bridging oxygen vacancies V. A pristine  $RuO_2(110)$  surface corresponds to vacant  $Ru_{cus}$  sites and all V sites covered with bridging oxygen atoms  $O_{br}$ . Surface densities of both types of sites are equal to  $8.3827 \times 10^{-10}$  mol/cm<sup>2</sup>. MKM simulations are carried out in a batch reactor mode. The reactor is modeled as a 60 L chamber containing a  $RuO_2(110)$  single crystal with a 78.5 mm<sup>2</sup> surface area. This corresponds to a surface area-to-volume ratio (A/V) of  $1.31 \times 10^{-5}$  cm<sup>-1</sup>. Simulation results are insensitive to specific A/V values. During 100 L H<sub>2</sub> exposure, a  $RuO_2(110)$  surface is in contact with  $1.33 \times 10^{-9}$  atm H<sub>2</sub> for 100 s at 25 °C.

Thermodynamic parameters of H<sub>2</sub> and H<sub>2</sub>O in a gas phase are taken from the Burcat database<sup>381</sup>. Formation energies of surface species and corresponding surface reaction energies are calculated with DFT by taking into account zero-point energy corrections and temperature effects. All surface species are assumed to have only vibrational degrees of freedom. Enthalpies and entropies of formation for all surface species are referenced to H<sub>2</sub> and H<sub>2</sub>O in the gas phase at 1 atm and 298.15 K to ensure thermodynamic consistency. Reaction barriers are approximated by the corresponding electronic energies from DFT, as obtained from nudged elastic band/dimer calculations. Therefore, cancellation of vibrational contributions from initial and transition states to Gibbs free energy barriers is assumed as a first approximation. Consequently, pre-exponential factors are taken as  $8.6 \cdot 10^{12}$  s<sup>-1</sup> (at 413.15 K). H<sub>2</sub>

adsorption on  $Ru_{cus}$  sites is assumed to be in equilibrium (sticking coefficient is assumed to be 1).

For the MKM, we initially included hydrogen dissociation and vacancy formation reactions on a pristine  $RuO_2(110)$  surface, DFT energetics for which has been published elsewhere<sup>4</sup>. Upon H<sub>2</sub> exposure, O<sub>br</sub> underwent complete conversion to hydroxyls OH<sub>br</sub> within 0.3 s of the reaction, in agreement with experiments<sup>137</sup>. Therefore, we used reaction energies and barriers on a fully hydroxylated  $RuO_2(110)$  surface in subsequent MKM simulations. Reaction barriers are reported in Table S6 (reactions 6-11); the THERMDAT file containing NASA polynomials, with thermodynamic information for all gas and surface species used in the model, is in attachment.

In Table B.8, we report simulated surface coverages at the end of the 100 s H<sub>2</sub> exposure period, in comparison with experimental values, obtained using XPS/STM<sup>137</sup>. As DFT overestimates binding of O-containing species on a vacancy by ~0.1 eV (Section B.1) and OH<sub>br</sub> dominates the surface, for the simulation we adjusted the OH binding energy by 0.1 eV. Results of MKM with non-modified and modified OH<sub>br</sub> binding energies are displayed in columns 2 and 3, respectively. After 100 s of H<sub>2</sub> exposure, 5% of OH<sub>br</sub> become vacancies, 5% of Ru<sub>cus</sub> sites become occupied by H<sub>2</sub>O, and H<sub>2</sub>O<sub>br</sub> coverage is negligible, in quantitative agreement with the experiment. The model also predicts that 1/3 of Ru<sub>cus</sub> sites are covered with H. The MKM results are consistent with facile vacancy formation on RuO<sub>2</sub>(110) at room temperature.

Reaction path analysis results are reported in Figure 3 of the main text. The model indicates that all surface reactions are equilibrated, except for H<sub>2</sub>O removal from the surface. Consequently, vacancy formation on  $RuO_2$  at given reaction conditions is governed by thermodynamics, not kinetics.

# Table B.8. Coverages of surface species after 100 L H2 exposure of RuO2(110) surface at 25 oC, as predicted by microkinetic model, in comparison with experimental data.

Surface species	Coverages predicted by first principles-		Experimental	
	based microkinetic model, %		coverages <sup>137</sup>	
	Pure DFT	OH <sub>br</sub> destabilized		
	energetics	by 0.10 eV		
Species on Ru <sub>cus</sub> sites				
H <sub>cus</sub>	30.5	29.4	N/A	
H <sub>2cus</sub>	$5.6 \cdot 10^{-7}$	$5.4 \cdot 10^{-7}$	N/A	
H <sub>2</sub> O <sub>cus</sub>	0.1	4.1	~ 5	
Rucus (vacant sites)	69.4	66.5	N/A	
O <sub>br</sub> -derived species				
Obr	$2.3 \cdot 10^{-4}$	0.01	~ 0	
OH <sub>br</sub>	99.9	95.1	~ 95	
H <sub>2</sub> O <sub>br</sub>	$9.9 \cdot 10^{-11}$	$4.5 \cdot 10^{-9}$	negligible	
Vacancies	0.1	4.9	~ 5	

We used predicted surface coverages as an input to the simulation of temperature-programmed desorption/reduction experiments. Evolution of H<sub>2</sub> and H<sub>2</sub>O products, as well as surface coverages of OH<sub>br</sub> and H<sub>2</sub>O<sub>cus</sub> are shown in Figure B.5. The model reproduces essential experimental features quite well <sup>137,398</sup>: H<sub>2</sub> desorption peak appears first, followed by two H<sub>2</sub>O formation peaks. The first H<sub>2</sub>O peak is associated with desorption of H<sub>2</sub>O<sub>cus</sub>; the second peak represents removal of O<sub>br</sub>H surface species, consistent with experimental findings<sup>137,398</sup>. The simulated H<sub>2</sub>O<sub>cus</sub> peak appears at ~50 K lower temperature than in the experiment, which corresponds to

underestimation of H<sub>2</sub>O binding energy by ~0.1 eV, according to the Redhead equation. Besides inaccuracy of DFT, the error is likely to be associated with adsorbed H<sub>2</sub>O possessing translational entropy, not accounted for in the model. Experimentally surface H<sub>2</sub>O is known to become mobile above 238 K, and is prone to form dimers on the RuO<sub>2</sub>(110) surface<sup>399</sup>.

It is important to note that at temperatures > 400 K  $OH_{br}$  undergoes rapid conversion to  $O_{br}$  and vacancies (Figure B.5). DFT calculations indicate that  $OH_{br}$ binds 0.3 eV stronger on an  $O_{br}$ -dominated surface, compared to the  $OH_{br}$ -covered one (Table B.2), the difference not accounted for in the MKM. Therefore, from the Redhead equation we estimate the second H<sub>2</sub>O peak to appear at ~120 K lower temperature in our model than in the experiment. Consistent with the estimate, the experimental H<sub>2</sub>O evolution rate peaks at 550-600 K vs. 415 K in the MKM. Complex shape and broad nature of the experimental peak<sup>137,398</sup> can in part be due to surface



Figure B.5. Simulated temperature programmed desorption/reduction profile, following 100 L  $H_2$  exposure of the RuO<sub>2</sub>(110) surface at ultrahigh vacuum conditions. Heating rate 10 K/s.

kinetics complicated by oxygen diffusion from the bulk  $RuO_2$  at high temperatures. Experimentally oxide film reduction outside the 2D surface region is substantial at >  $200^{\circ}C^{400}$ ; computationally we found the reaction barrier for diffusion of the O atom underneath the vacancy to the surface to be equal to 0.9 eV (surface with 100% vacancies), comparable with certain surface reaction barriers, e.g., H<sub>cus</sub> reactions with O<sub>br</sub> and OH<sub>br</sub>.

#### B.4 Microkinetic Model of Furfuryl Alcohol Hydrogenolysis in a Batch Reactor

### **B.4.1 Model Specifications**

The purpose of this model is to determine whether the radical C-O bond hydrogenolysis mechanism on  $RuO_2$  vacancies, formed using  $H_2$  produced on metallic sites, is consistent with batch reactor data, published previously<sup>110</sup>.

In the MKM, we assume that Ru and RuO<sub>2</sub> catalytic surfaces are spatially separated and only communicate with each other through the bulk liquid phase, i.e., no spillover of surface species is involved and no Ru/RuO<sub>2</sub> interfacial sites are included. The MKM solution involves two steps: (1) calculation of the effective first-order H<sub>2</sub> generation rate constant for 2-propanol dehydrogenation on metallic Ru(0001), with competitive adsorption of the toluene solvent, furfuryl alcohol, and 2-methyl furan from the liquid phase taken into account; (2) solution of the MKM for furfuryl alcohol hydrogenolysis on RuO<sub>2</sub>(110); the 2-propanol dehydrogenation to acetone and H<sub>2</sub> is included with an effective rate constant found in step 1.

Chemical potentials of the liquid reaction mixture are calculated with ASPEN Plus V.8.6 software. Activity coefficients are estimated using the UNIQUAC method. Since the effect of activity coefficient changes as a function of a mixture composition is small (<0.02 eV change in chemical potentials, well within DFT accuracy), activity coefficients are calculated at a fixed mixture composition, equivalent to 10% conversion of furfuryl alcohol to 2-MF. As 2-MF UNIQUAC parameters were not available in the database, we estimated them by assuming that the compound behaves similarly to tetrahydrofuran (THF), when mixed with toluene and 2-propanol. We found the THF activity coefficient to be in a range of 0.6-0.9 at temperatures 25-200 °C, providing <0.02 eV correction to a pure component chemical potential.

Prior to a typical MKM run, we use ASPEN to calculate molar amounts of components constituting 24 mL of a mixture initially loaded into the reactor (1 wt. % of furfuryl alcohol mixed with a solvent consisting of 10 vol. % 2-propanol and 90 vol. % toluene). Then we set up a batch reactor in ASPEN and calculate the amount of  $N_2$  to be added to reach the initial reactor pressure of 2.04 MPa at 25 °C. We fix the number of  $N_2$  moles and bring the reactor to its operational temperature (140 °C). Finally, we use the predicted reactor pressure (3.49 MPa), liquid phase volume (27.5 mL), and the composition of the liquid phase (0.849 mol. % furfuryl alcohol, 11.9 mol. % 2-propanol, and 87 mol. % toluene) at 140°C as the MKM input. Although three phases are present during the reaction, we neglect vapor-liquid equilibrium and only consider two phases in the MKM (the surface and the liquid bulk).

To estimate the number of catalytic sites in the reactor, we use chemisorption data by Jae et al.<sup>175</sup> (0.00022 mol CO/g catalyst after reduction; the Ru/C catalyst contained 4.63 wt.% of Ru). Further, we assume 1-to-1 equivalence between metallic Ru sites of the reduced catalyst and Ru<sub>cus</sub> sites of RuO<sub>2</sub>. Surface site density is assumed equal to that on an ideal RuO<sub>2</sub>(110) surface (8.38 10<sup>-10</sup> mol/cm<sup>2</sup>). This gives

the surface area-to-volume ratio in the reactor equal to  $9.54 \cdot 10^2$  cm<sup>-1</sup>. Finally we further assume that the catalyst surface involves Ru and RuO<sub>2</sub> surface areas at the ratio of  $3 \cdot 10^{-4}$ , yielding the predicted furfuryl alcohol hydrogenolysis rate to be equal to the experimentally measured one (see the main text).

The 2-propanol dehydrogenation MKM on Ru(0001) uses thermodynamic and kinetic parameters reported previously<sup>5</sup>. Only 2-propanol dehydrogenation to acetone and (co)adsorption steps of bulk species are included. Two types of sites are considered – one for bulky C-containing species, and another one for H atoms. In the model, every 2-propanol-derived compound occupies 4 sites, adsorbed furfuryl alcohol -5 sites, adsorbed toluene -6 sites<sup>5</sup>. Since no gas phase is included in the MKM, the low H<sub>2</sub> solubility in the liquid leads to the 2-propanol dehydrogenation equilibrium shifted toward the reactant ( $K_a = 3.4 \cdot 10^{-10}$ ), with the maximum reactant conversion not exceeding ~1%. Contrary to the model, the experimental 2-propanol conversion to acetone and  $H_2$  can reach ~20% on the Ru/C catalyst, with the majority of H<sub>2</sub> partitioned to the gas phase inside the reactor, according to ASPEN simulations. In addition, low experimentally observed 2-propanol conversion (<3-5%) indicates that 2-propanol dehydrogenation is far from equilibrium. In order to account for the model deficiency, we added the fast  $FCH_2OH+H_2 \rightarrow FCH_3+H_2O$  reaction in the bulk phase, which rapidly consumes H<sub>2</sub> and shifts the equilibrium towards the products, allowing us to calculate the H<sub>2</sub> production rate. The sensitivity analysis (see below) indicates that the hydrogen production is the rate-limiting step and the HDO chemistry is fast, validating the reaction choice. Figure B.6 shows the linear decrease of the 2propanol molar fraction with time due to its conversion to acetone and H<sub>2</sub>; the corresponding effective rate constant for H<sub>2</sub> production on metallic Ru sites is also shown.



Figure B.6. Simulated 2-propanol consumption as a function of time.

We model RuO<sub>2</sub>(110) with two types of sites (cus sites and vacancies; see Section B.3). Every surface species is assumed to occupy a single site on the surface. Formation energies of surface species and corresponding surface reaction energies are calculated using DFT and include zero-point energy corrections and temperature effects. All surface species are assumed to have only vibrational degrees of freedom. Enthalpies and entropies of formation for all surface species are referenced to H<sub>2</sub>, H<sub>2</sub>O, and furfuryl alcohol in the gas phase at 1 atm and 298.15 K to ensure thermodynamic consistency. Reaction barriers are approximated by the corresponding electronic energies from DFT, as obtained from nudged elastic band/dimer calculations. Therefore, cancellation of vibrational contributions from initial and transition states to Gibbs free energy barriers is assumed as a first approximation, which should be reasonable, due to a weak interaction of furanic intermediates with RuO<sub>2</sub>(110). Consequently, pre-exponential factors are taken as 8.6 10<sup>12</sup> s<sup>-1</sup> (at 413.15 K). Elementary steps of furfuryl alcohol conversion to 2-MF on a vacancy are treated as first order processes. Reaction barriers are reported in Table B.6; the THERMDAT files containing NASA polynomials with thermodynamic information for all gas and surface species are attached.

We only consider two types of lateral interactions between surface species: 2propanol/2-propanol interaction on cus sites (type 1), and the effect of 2-propanol coadsorption on the FCH<sub>2</sub>OH<sub>br</sub> binding energy (type 2). The effect of co-adsorbed 2propanol on propoxy species and adsorbed acetone was assumed to be similar to the 2propanol/2-propanol interaction. Energetics of all surface species derived from furfuryl alcohol was modified due to the presence of co-adsorbed 2-propanol in a same way as the furfuryl alcohol binding energy.

For type 2 lateral interactions, changes of furfuryl alcohol differential adsorption energy with coverage were calculated as its binding energy on a  $RuO_2(110)$  slab pre-occupied with 1, 2, 3, 4, or 5 2-propanol molecules. For type 1 lateral interactions, we first calculated average binding energies at different 2-propanol coverages as

$$BE_{av}(\theta) = \frac{E_{nIPA} - E_{slab} - n \times E_{IPA,vacuum}}{n};$$

Here  $BE_{av}(\theta)$  is an average 2-propanol binding energy as a function of coverage;  $E_{nIPA}$  is the energy of the RuO<sub>2</sub>(110) slab with *n* adsorbed 2-propanol (IPA) molecules;  $E_{slab}$  is the energy of the pristine slab;  $E_{IPA,vacuum}$  is the energy of the 2-propanol molecule in vacuum. Then the integrated adsorption energy at several coverages (0.17, 0.33, 0.5, 0.67, 0.83 ML) was calculated as

$$\Delta E_{int} = BE_{av}(\theta) \times \theta$$

Finally, the (minus) differential heat of adsorption was calculated using a finite difference method:

$$\Delta E_{diff} = \frac{dE_{int}}{d\theta} \Big|_{\left(\frac{\theta_{i+1}+\theta_i}{2}\right)} = \frac{E_{int,i+1}-E_{int,i}}{\theta_{i+1}-\theta_i}$$

The resulting values are reported in Figure B.7.



Figure B.7. Type 1 and type 2 lateral interactions, modeled using a piecewise linear model. Differential adsorption energies are shown as a function of 2-propanol coverage

## **B.4.2** Analysis of MKM Results

Table B.9 reports normalized sensitivity coefficients, indicating that the overall hydrogenolysis rate is governed by hydrogen production on metallic Ru sites. As this fact has implications on simulated reaction orders and the apparent activation energy, Here we discuss the 2-propanol dehydrogenation mechanism in detail.

Table B.9. Normalized sensitivity coefficients for various reactions in the hydrogenolysis mechanism of Table B.6. Pre-exponential factors were perturbed by a factor of 2, equivalent to ~0.02 eV barrier perturbation.

Reaction	Normalized
	sensitivity
	coefficient
ACHOH=ACO+H <sub>2</sub>	1
FCH <sub>2</sub> OH <sub>br</sub> =FCH <sub>2</sub> -OH <sub>br</sub>	0.0020
$FCH_2-OH_{br} = FCH_2-HO_{br}$	0.0012
H <sub>2,cus</sub> +OH <sub>br</sub> =H <sub>cus</sub> +H <sub>2</sub> O <sub>br</sub>	0.0001
H <sub>cus</sub> +OH <sub>br</sub> =Ru <sub>cus</sub> +H <sub>2</sub> O <sub>br</sub>	0.0009
H <sub>2,cus</sub> +O <sub>br</sub> =H <sub>cus</sub> +OH <sub>br</sub>	2.10-5
H <sub>cus</sub> +O <sub>br</sub> =Ru <sub>cus</sub> +OH <sub>br</sub>	0.0085
$H_2O_{br}=V+H_2O$	7.10 <sup>-7</sup>
$V-H_2O_{cus}=V+H_2O$	1.10-6
$H_2O_{br}+Ru_{cus}=V-H_2O_{cus}$	1.10-6

Figure B.8 displays the Gibbs free energy pathway for the 2-propanol dehydrogenation mechanism on Ru(0001). The process begins with 2-propanol

adsorption, followed by O-H scission, C-H scission, and finally the desorption of acetone and hydrogen. The mechanism exhibits two irreversible steps, according to the partial equilibrium values (these values show the degree of reversibility of an elementary reaction): O-H bond scission and hydrogen desorption. Among these two steps, hydrogen desorption is not the rate-limiting one, since no site blocking by H occurs (Table B.10; type 2 vacant site coverage is significant). Consequently, the only option for the rate-controlling step is the O-H bond scission. This is consistent with the observed kinetic isotope effect of 1.6 for CH<sub>3</sub>CH(OH)CH<sub>3</sub> vs. CH<sub>3</sub>CH(OD)CH<sub>3</sub> on Ru-based catalysts<sup>146,401</sup>. Knowledge of the rate-determining step allows us to derive a simplified rate expression:

$$r = A \times e^{-\frac{\Delta H_{app}}{RT}} \times \left(\frac{C_{IPA}}{C_0}\right) \times \theta_*^4 \tag{1}$$

Here A is the pre-exponential factor that accounts for entropic effects;  $\theta_*$  is the coverage of type 1 vacant sites (the power of 4 is due to adsorbed 2-propanol occupying 4 surface sites);  $C_{IPA}$  is the bulk concentration of 2-propanol;  $C_0$  is the reference concentration;  $\Delta H_{app} = \Delta H_{ads,IPA} + \Delta H_{0-H}^{\neq}$  is the apparent activation energy at  $\theta_*=1$ ;  $\Delta H_{ads,IPA}$  is the adsorption enthalpy of IPA;  $\Delta H_{0-H}^{\neq}$  is the reaction barrier of the rate-determining step (O-H bond scission).


Figure B.8. Gibbs free energy pathway for 2-propanol dehydrogenation on Ru(0001). Energies are calculated at 413.15 K, in the presence of 0.78 ML of the co-adsorbed toluene solvent. Desorbed species energies are given for the liquid phase. Partial equilibrium values (PE), calculated for each elementary step as a ratio of the forward reaction rate to the sum of the forward and the backward reaction rates, are shown on top of the lines. PE = 0.5 corresponds to an equilibrated step; PE = 1 -to an irreversible step.

Table B.10. Surface coverages on Ru(0001) at the end of the 5-hour period.

	Surface coverages,
	ML
Species on type 1 sites (C-containing species)	
Furfuryl alcohol	0.22
Toluene	0.61
2-propoxy (CH <sub>3</sub> CH(O)CH <sub>3</sub> )	0.15
Type 1 vacant sites	0.01
Other species	< 0.01
Species on type 2 sites (available for H only)	
H	0.31
Type 2 vacant sites	0.69

### **B.4.3 Reaction Order with respect to 2-propanol**

The rate of  $H_2$  production and the overall hydrogenolysis rate as a function of the 2-propanol concentration are shown in Figure B.9, yielding the reaction orders of 0.60 and 0.61, respectively. Similar reaction-order values are consistent with the furfuryl alcohol hydrogenolysis governed by the  $H_2$  production on Ru(0001). Differences in y-axis values between (a) and (b) are due to hydrogenolysis catalyzed by RuO<sub>2</sub>(110) to a small extent in the absence of Ru, as well as the H<sub>2</sub> production and hydrogenolysis steps in the MKM being decoupled. Figure B.9 also implies the reaction order with respect to  $H_2$  would be unity, if  $H_2$  is used instead of 2-propanol. Previously,  $H_2$  reaction orders of 0.8-1.0 were observed in other C-O bond hydrogenolysis chemistries, such as ring opening in tetrahydrofurfuryl alcohol on



Figure B.9. H<sub>2</sub> production rate on Ru(0001) (a) and furfuryl alcohol hydrogenolysis rate on RuO<sub>2</sub>(110) (b) as a function of 2-propanol concentration. r is in mol  $L^{-1}h^{-1}$ ; C<sub>0</sub> is in mol/L.

 $Ir/ReO_x^{109}$  and furfural hydrogenolysis on a Cu-based catalyst<sup>156</sup>.

Deviation of the 2-propanol reaction order from unity can be explained using equation 1. Upon increase of the alcohol concentration by a factor of 2.17, the dehydrogenation rate becomes greater only by a factor of 1.6. At the same time, the surface coverage of propoxy increases from 0.11 to 0.16 ML, influencing coverages of other surface species, including type 1 empty sites, which decrease from 0.0143 to 0.0130 ML. This slight change in the coverage of the empty sites has a significant effect on the rate, due to the forth power dependence (equation 1). Specifically, at 2.17-fold increase of 2-propanol concentration,  $\theta_*^4$  lowers by a factor of 0.69, causing a deviation of the reaction order from unity. Interestingly, lower reaction orders (<0.3) were observed during 2-propanol dehydrogenation on supported Cu catalysts<sup>402</sup>, despite weaker binding of surface intermediates on Cu. Such reaction order differences may be due to solvent effects. On Ru(0001), strong lateral interactions with the co-adsorbed solvent (toluene; 0.61 ML coverage) lower binding energies of surface intermediates by 0.6 eV, preventing further blocking of surface sites. It is also possible that the actual 2-propanol reaction order is lower, due to limitations of the model<sup>5</sup>, causing overestimation of lateral interactions.

The rate of  $H_2$  production and the overall hydrogenolysis rate as a function of the furfuryl alcohol concentration are shown in Figure B.10, yielding negative reaction orders of -0.57 and -0.62, respectively. Similar reaction order values are consistent with the furfuryl alcohol hydrogenolysis governed by the  $H_2$  production on Ru(0001). If the effect of furfuryl alcohol on the  $H_2$  production rate is neglected in the model, then the reaction order of the hydrogenolysis reaction on RuO<sub>2</sub> vacancies become close to zero (-0.05). Previously, close to zero reaction orders were observed in other C-O bond hydrogenolysis chemistries, such as ring opening in tetrahydrofurfuryl alcohol on  $Ir/ReO_x^{109}$  and furfural hydrogenolysis on a Cu-based catalyst<sup>156</sup>.



Figure B.10. H<sub>2</sub> production rate on Ru(0001) (a) and furfuryl alcohol hydrogenolysis rate on RuO<sub>2</sub>(110) (b) as a function of furfuryl alcohol concentration. r is in mol  $L^{-1}h^{-1}$ ; C<sub>0</sub> is in mol/L.

Negative reaction order for the  $H_2$  production rate is consistent with the fact that the hydrogen production rate drops by a factor of 10, if furfural or furfuryl alcohol is added into the reaction mixture containing 2-propanol and the Ru/C catalyst<sup>111</sup>. The effect can be explained by looking at the evolution of surface species coverages with concentration (Figure B.11). At high bulk concentration of furfuryl alcohol, it becomes the dominant species on the surface, replacing 2-propoxy and also reducing

the number of surface empty sites. For example, if furfuryl alcohol concentration increases by a factor of 2.08 (from 0.0436 to 0.0909 mol/L), the empty site coverage reduces from



Figure B.11. Coverages of dominant surface species as a function of furfuryl alcohol concentration.

0.0142 to 0.0127, which translates to the reduction of  $\theta_*^4$  by a factor of 0.52. This accounts for the majority of the rate reduction (factor of 0.69 lower), resulting in the negative reaction order.

In Figure B.12, we report the rate of 2-propanol dehydrogenation and furfuryl alcohol hydrogenolysis as a function of temperature, yielding the apparent activation energies of 28.4 and 23.1 kcal/mol, respectively. High apparent activation energies for 2-propanol dehydrogenation are quite typical; for example, energies of 20-28 kcal/mol were reported for 2-propanol dehydrogenation on copper<sup>402</sup> and in hydrogenation of acetophenone on Ni/SiO<sub>2</sub> in the presence of the 2-propanol solvent (28 kcal/mol)<sup>403</sup>, where the promoting effect of the latter has been associated with its hydrogen donor activity. High activation energies can be explained through desorption of furfuryl alcohol at higher temperatures and increase in a vacant site coverage, leading to higher reaction rates. Interestingly, in the previous study of the catalytic transfer hydrogenolysis of furfuryl alcohol in 2-propanol, the dependencies of acetone and 2-methyl furan yields on temperature are equivalent to activation energies of 14.8 and 12.2 kcal/mol<sup>37</sup>, which are by a factor of two lower than the values found in the current study. This may be an indication of the experiments performed in the diffusion-controlled regime.



Figure B.12. First order 2-propanol dehydrogenation rate constant (a) and furfuryl alcohol hydrogenolysis rate constant (b) as a function of R-1T-1. k is reported in h-1.

### **B.4.4 Isotopic Labeling MKM**

In MKM for H/D labeling, we assumed that all deuterated species possess energetics identical to their non-deuterated counterparts. Doubly deuterated furfuryl alcohol FCHDOD is used as a feed, since it is experimentally produced in an MPVhydride transfer reaction RuO<sub>2</sub> Lewis acid type on sites: FCHO+ACDOD=FCHDOD+ACO, where FCHO is furfural, ACDOD is deuterated 2propanol, and ACO is acetone. If no D incorporation into the ring occurs, the reaction would proceed as FCHDOD+ACDOD=FCHD<sub>2</sub>+D<sub>2</sub>O+ACO, yielding a doubly deuterated 2-MF with a molecular weight of 84 amu. D substitution into the ring would correspondingly lead to a triply deuterated 2-MF (85 amu). The MKM indicates that the ratio between doubly and triply-deuterated 2-MF is approximately 2:1. To simulate the mass spectrum of the mixture, we considered contributions of individual isotopically labeled 2-MF compounds into the overall spectrum using a method

outlined at<sup>5</sup>. The -1 and -2 amu peaks relative to a molecular ion were adjusted from that of pure 2-MF to reflect different H:D ratios in a methyl group.



Figure B.13. Spin density plot for the pristine RuO<sub>2</sub>(110) surface.

### Appendix C

## FUNDAMENTALS OF C-O BOND ACTIVATION ON METAL OXIDE CATALYSTS

## C.1 Sensitivity Analysis in the Microkinetic Model for Furfural Conversion to 2methyl Furan on the Ru/RuO<sub>2</sub> Catalyst

In this section, we describe results of the sensitivity analysis applied to our previously reported microkinetic model<sup>8</sup> to reveal design criteria for more active C-O bond scission catalysts. Semi-normalized sensitivity coefficients are defined as the following:

$$S_i = \frac{\partial r_{MF}}{\partial \ln P_i} \tag{C.1}$$

Here  $r_{MF}$  denotes the 2-methyl furan (MF) formation rate,  $P_i$  – a parameter governing the rate of the elementary reaction *i* or its reverse, and  $S_i$  is the sensitivity coefficient for the reaction *i* with respect to the parameter  $P_i$ . The largest absolute value of  $S_i$  indicates that  $P_i$  has the largest impact on the 2-methyl production rate. We consider two types of parameters  $P_i$  – elementary reaction barriers and formation enthalpies of surface species.

In comparison with the original model, we reduced the catalyst surface-tovolume ratio from  $9.45 \cdot 10^2$  to  $9.45 \cdot 10^{-1}$  cm<sup>-1</sup>. This modification had no impact on intrinsic kinetics. All species enthalpies and reaction barriers were perturbed by 3 kcal/mol, one parameter at a time. In Tables C.1 and C.2, we report the largest  $S_i$  values (raw and normalized by the largest value) among the subset of reactions/species relevant to the C-O bond activation chemistry (i.e., furfuryl alcohol (FA) conversion to MF). The OH<sub>br</sub> formation enthalpy (relative to a vacancy, H<sub>2</sub>, and H<sub>2</sub>O) exhibits the largest  $S_i$ ; its positive sign indicates that its lower thermodynamic stability would expectedly lead to higher MF formation rates via vacancy formation promotion. To relate MF production rate changes to those of the M-O bond strength and account for energy correlations among surface species, we consider the following thought experiment.

Table C.1. Sensitivity coefficients for perturbations of species enthalpies

Surface species with the largest sensitivity	S <sub>i</sub>	Normalized unsigned <i>S<sub>i</sub></i>
OH <sub>br</sub>	1.55E-08	1.00
FCH <sub>2</sub> OH <sub>br</sub>	-9.66E-09	0.62
$FCH_{2}\boldsymbol{\cdot}-OH_{br}$	-5.24E-09	0.34
IPAcus	2.99E-09	0.19
H <sub>2</sub> O <sub>cus</sub>	-2.18E-09	0.14

"br" stands for sites corresponding to bridging oxygen atoms on the pristine  $RuO_2(110)$  surface; "cus" – coordinatively unsaturated Ru atoms (Lewis acid sites);  $FCH_2OH$  – furfuryl alcohol;  $FCH_2$ · –  $OH_{br}$  – a pair of a furfuryl radical and a proximal OH group, formed after C-O bond scission in  $FCH_2OH_{br}$ ; IPA – 2-propanol.

Elementary reactions with the largest sensitivity	$S_i$	Normalized unsigned $S_i$
$FCH_2OH_{br} \rightarrow FCH_2 \cdot - OH_{br}$	-9.66E-09	0.62
$FCH_2 \cdot - OH_{br} \rightarrow FCH_2 \cdot -$		
HO <sub>br</sub>	-5.24E-09	0.34
$FCH_2 \cdot - HO_{br} \rightarrow FCH_{3,br}$	-5.85E-10	0.04
$H_{cus}+OH_{br}\rightarrow H_2O_{br}$	-9.70E-11	0.01

Table C.2. Sensitivity coefficients for perturbations of reaction energy barriers

Reaction 2 depicts surface OH group rotation

#### preceding FCH<sub>3</sub> formation

We envision a RuO<sub>2</sub>-like catalyst, but with weaker covalent M-O bonds. Evidently, weakened bonds will translate to lower stability of covalently bound surface species among those in Table C.1 and C.2, in particular OH<sub>br</sub> and FCH<sub>2</sub>· – OH<sub>br</sub>, as well as of transition states for all four reactions. Reported  $S_i$  values indicate that two opposite effects will be observed – weaker binding of OH<sub>br</sub> will increase the reaction rate, whereas weaker binding of all other species will decrease it. However, the OH<sub>br</sub> rate acceleration effect will prevail, as follows from the following argument. The transition state of the reaction 1 (Table C.2) that corresponds to the second highest  $S_i$  among both tables, is structurally similar to the FCH<sub>2</sub>· – OH<sub>br</sub> state<sup>8</sup>, and thus its energy should linearly correlate with that of the latter via the Brønsted-Evans-Polanyi relationship<sup>404</sup> with the slope  $\leq 1^{405}$ . Since the FCH<sub>2</sub>· – OH<sub>br</sub> state involves the OH<sub>br</sub> enthalpy should be linearly related to that of  $OH_{br}$  with the slope of approximately 1. As a result, the destabilization of  $OH_{br}$  will lead to similar or lower destabilization of the C-O scission transition state. Since the latter exhibits a lower sensitivity coefficient, we conclude that the net effect of the M-O bond weakening will be the higher C-O scission rate.

## C.2 Computation of Thermodynamic Properties of the Reaction Mixture at Experimental Conditions

The chemical equilibrium condition at given T and P for a single reaction in a single phase is

$$\sum v_i \overline{G}_i = 0 \tag{C.2}$$

Here  $v_i$  are stoichiometric coefficients of a chemical reaction and  $G_i$  are partial molar Gibbs free energies of species. By expanding the latter as  $\overline{G}_i = \underline{G}_i + G_{i,ex} + RT \ln x_i$ , where  $\underline{G}_i$  and  $G_{ex}$  are the pure component and excess molar Gibbs free energy, respectively, and  $x_i$  is the molar fraction of the compound *i*, we obtain

$$-\sum \frac{\nu_i (\underline{G}_i + G_{i,ex})}{RT} = \ln \prod_i x_i^{\nu_i}$$
(C.3)

The expression  $(\underline{G}_i + G_{i,ex})$  defines the partial molar Gibbs free energy (chemical potential) of species *i* at  $x_i = 1$ , that we denote as  $\overline{G}_i(x_i = 1)$ . The right-hand side of the equation (C.3) defines the equilibrium constant in concentration units,

which is employed in calculations of reverse rate constants via the microscopic reversibility  $k_{rev} = \frac{k_f}{K_c}$  in CHEMKIN<sup>64</sup>. Therefore, in order to calculate  $K_c$  correctly, accurate estimates of pure component and excess Gibbs free energies (defining species chemical potentials at  $x_i = 1$ ) at experimental reaction conditions are necessary.

We employ ASPEN Plus V8.6 software to calculate chemical potentials of reactants and products, including H<sub>2</sub> chemical potential, under the reaction conditions to be used in the  $TiO_2$  microkinetic model (Section C.4) and *ab initio* thermodynamics calculations for surface termination (Section C.3). The UNIQUAC model was utilized to calculate activity coefficients. The overall procedure consists of three steps.

In the first step, we calculate the composition of the liquid phase inside the reactor using the flowchart depicted in Figure C.1. The scheme consists of the RBatch module B4 (160 mL volume), separator B5, and two mixers B1 and B2. No chemical reactions are included in RBatch. Compositional dependence of activity coefficients is neglected in this study, as reaction rate measurements are performed at <15% conversions. Since no UNIQUAC parameters are available for 2MF, we approximate its activity coefficient by that of tetrahydrofuran. As the activity coefficients for all species in the mixture, except water, lie in the range of 0.39-1 (*vide infra*), we anticipate the error in the 2MF chemical potential due to such replacement to be < 0.04 eV.

The initial batch loading consists of material flows S1, S2, and S10. S10 represents liquid mixture composed of 100 mL toluene and 0.98 g FA, i.e., 0.940959 mol of toluene and 0.009990 mol of FA. In the ASPEN model, we assume 10% conversion of FA and 100% selectivity to 2MF and H<sub>2</sub>O. S1 and S2 material flows involve 4.7 bar H<sub>2</sub> and 15 bar N<sub>2</sub>, respectively, at 298 K. Initially, we set the reactor

temperature to 25 °C, the N<sub>2</sub> flow rate to zero, and adjust the H<sub>2</sub> volume to 0.063 L (4.7 bar, 298 K) such that the pressure inside the reactor equals 4.7 bar. We subsequently increase the reactor temperature to 433 K, - the total pressure becomes 12.8427 bar. Finally, we adjust the N<sub>2</sub> volume to 0.0064 L (15 bar, 298 K) in order to reach the total reactor pressure of 15 bar. The reactor output S7 enters the separator B5, maintained at 15 bar and 433 K. The composition of the liquid phase S9 and the molar percentage of the total amount of a particular species present in the liquid phase



Figure C.1. ASPEN flowchart used in chemical potential calculations inside the batch reactor.

as predicted by ASPEN are reported in Table C.3.

Substance	Liquid phase	Molar % of the
	molar fraction	substance total amount
		present in the liquid
		phase
FA	$9.45 \cdot 10^{-3}$	99.7
Toluene	0.986	98.8
$H_2$	$1.63 \cdot 10^{-3}$	4.69
$N_2$	$1.32 \cdot 10^{-3}$	17.0
$H_2O$	$6.47 \cdot 10^{-4}$	34.6
2MF	$1.04 \cdot 10^{-3}$	96.6

Table C.3. Composition of the reactor content at 433 K and 15 bar

In the second step, we compute pure species enthalpies and entropies of formation, their constant-pressure molar heat capacities, and activity coefficients at the given mixture composition (Table C.3) at 100 temperature values in the range of 25-200  $^{\circ}$ C.

In the third and final step, we calculate excess properties as a function of temperature as the following (herein standard thermodynamic notation is used):

$$G_{ex,i}(T) = RT \ln \gamma_i(T) \tag{C.4}$$

$$H_{ex,i}(T) = -RT^2 \frac{d\ln\gamma_i(T)}{dT}$$
(C.5)

$$S_{ex,i}(T) = \frac{H_{ex,i}(T) - G_{ex,i}(T)}{T}$$
(C.6)

$$c_{p,ex,i}(T) = \frac{dH_{ex,i}(T)}{dT}$$
(C.7)

In equations C.5 and C.7, the derivatives are computed using the finite difference method. Excess properties are then added to the corresponding pure component properties to obtain  $\overline{\theta}_i$  (*vide supra*). Subsequently,  $\overline{H_i}(298 K)$ ,  $\overline{S_i}(298 K)$ , and  $\overline{c_{p,i}}(T)$  in the range of 25-200 °C are converted to NASA polynomials, and their coefficients are used as an input to the CHEMKIN-based in-house code<sup>63,64</sup>.

### C.3 Surface-termination Determination Procedure

We find the H<sub>2</sub> chemical potential under the reaction conditions to be equal to -0.1078 eV relative to the value at 25 °C and 1 bar. For comparison, the chemical potential of the H<sub>2</sub> ideal gas at 433 K and 7 bar is -0.1178 eV.

In order to determine equilibrium surface terminations, we employ stationary properties of the total Gibbs free energy of the closed system (surface +  $H_2$  reservoir) at fixed T and P. We consider the following chemical reaction between an oxide surface and  $H_2$ :

$$MO_x + \frac{y}{2}H_2 = MO_xH_y$$

The Gibbs free energy of the reaction is

$$G_{rxn} = \bar{G} \left( M O_x H_y \right) - \bar{G} \left( M O_x \right) - \frac{y}{2} \bar{G} (H_2)$$
(C.8)

We assume that the H<sub>2</sub> chemical potential is fixed, so y is the only independent variable. At equilibrium  $G_{rxn}$  is minimized, provided that the surface area is constant.<sup>406</sup> We calculate  $\bar{G}(MO_xH_y)$  at various values of y from DFT;  $MO_xH_y$ 

corresponding to the lowest  $G_{rxn}$  represents the most thermodynamically stable surface termination at reaction conditions. In choosing which structures to compute, we make an assumption that at low coverages, H binds only to the most coordinatively unsaturated surface O atoms (such as bridging O<sub>br</sub>), whereas at high coverages binding to both M and O site types occur. Preliminary tests for a selected number of structures indicate that this is a reasonable assumption – O sites exhibit much greater hydrogen affinity compared to M sites.

The  $G(H_2)$  value was obtained using ASPEN Plus at experimental reaction conditions, as described in Section C.2. When calculating non-electronic contributions to the  $\bar{G}(MO_xH_y) - \bar{G}(MO_x)$  Gibbs free energy difference, we assume that only vibrational degrees of freedom are present, which are in turn described by Einstein crystal model, i.e., vibrations of every surface H atom are decoupled. We further assume exact cancellation of vibrational contributions due to M and O. In addition, we neglect the configuration entropy contribution to Gibbs free energies of slabs with partial monolayer adsorbate coverages. The quantity  $TS_{conf} = Tk_B \ln \frac{M!}{N!(M-N)!} =$  $-Tk_B M[x \ln x + (1 - x) \ln(1 - x)]$ , where  $k_B$  is the Boltzmann constant, M is the total number of sites, N is the number H atoms occupying the sites, and  $x = \frac{N}{M}$ , takes values <0.10-0.21 eV per slab for slabs containing 4-8 sites, which is considerably smaller than typical energy differences for various structures considered, except for SnO<sub>2</sub> and VO<sub>2</sub> (*vide infra*).

The resulting expression for the Gibbs free energy difference is the following:

$$\bar{G}(MO_xH_y) - \bar{G}(MO_x)$$
  
=  $E_{DFT}(MO_xH_y) - E_{DFT}(MO_x) + yE_{vib,H}(MO_xH_{y'})$  (C.9)

Here  $E_{DFT}$  are DFT electronic energies of a non-hydrogenated and hydrogenated slab, respectively, and  $E_{vib,H}$  is the vibrational energy associated with a single surface H atom on a representative  $MO_xH_{yi}$  structure. A single H atom was relaxed in every vibrational frequency calculation, except for IrO<sub>2</sub>(110) and ZnO(1010), for which one H<sub>M</sub> and one H<sub>O</sub> atom were relaxed. For MoO<sub>3</sub>(100), the vibrational contribution per H<sub>M</sub> atom was taken as an average over H<sub>M</sub> contributions for all other oxide surfaces. This approximation has no consequences on surface termination predictions, since H<sub>M</sub> is very unstable. Hydrogen vibrational contributions on IrO<sub>2</sub>(101), IrO<sub>2</sub>(100), RuO<sub>2</sub>(101), RuO<sub>2</sub>(100), and TiO<sub>2</sub>(100) were assumed to be the same as on corresponding (110) surfaces.



Figure C.2. Gibbs free energies of formation of hydrogenated surfaces relative to pristine ones and experimental  $H_2$  chemical potential.

Figure C.2 depicts Gibbs free energies of formation of hydrogenated surfaces, described by equation C.8. Structures with the lowest formation energies are encircled. The most stable surface terminations are summarized in Figure 4.4 of the main manuscript. For  $SnO_2(110)$ , the PBE+U functional predicts the structures with various H coverages to lie energetically close to each other (Figure C.2i). Since the U parameter has been calculated for the bulk  $SnO_2^{214}$ , and the U parameter dependence on geometry has been reported<sup>350</sup> (i.e., the bulk and the surface may require different U values), there is an uncertainty in surface termination predictions on  $SnO_2(110)$ using the PBE+U method. To resolve this, we employed the PBE functional instead (Figure C.2j), which revealed the structure with 1 ML H<sub>0</sub> and 0 ML H<sub>M</sub> coverages to be most likely present under the experimental conditions. Similar to  $SnO_2(110)$ , various H coverages on VO<sub>2</sub>(110) are energetically close (Figure C.2h). We computed OH recombination/vacancy formation energies on 0.33 ML and 1 ML Ho-covered surfaces and obtained almost identical values (0.92 and 0.91 eV, respectively). We conclude that the near-degeneracy for various H coverages on  $VO_2(110)$  has no effect on vacancy formation energetics.

# C.4 Mirokinetic Model for C-O Scission in Furfuryl Alcohol on TiO<sub>2</sub>(110) Vacancies

### C.4.1 Reaction Network

The TiO<sub>2</sub>(110) surface involves pairs of the following catalytic sites: coordinatively unsaturated, Lewis-acidic metal atoms  $M_{cus}$  and bridging oxygen atoms  $O_{br}$  (Figure C.3). The pristine surface corresponds to 1 monolayer (ML) coverage of empty sites  $M_{cus}$  and 1 ML of  $O_{br}$  on oxygen vacancies, denoted as  $V_{br}$ . A list of allowed species in the microkinetic model (MKM) that can occupy either  $M_{cus}$  or  $V_{br}$ sites is the following:

### Mcus sites:

- M<sub>cus</sub> (empty site)
- H<sub>cus</sub>
- H<sub>2,cus</sub>
- FA<sub>cus</sub> (furfuryl alcohol)

FAmH<sub>cus</sub> (furfuryloxy)

<u>Vbr sites:</u>

- V<sub>br</sub> (vacancy)
- O<sub>br</sub>
- OH<sub>br</sub>
- H<sub>2</sub>O<sub>br</sub>
- FA<sub>br</sub>
- (MF+O)<sub>br</sub> (2-methyl furan physisorbed on O<sub>br</sub>)



Figure C.3. Two types of catalytic sites on the  $TiO_2(110)$  surface

The list of the allowed reactions with the corresponding DFT electronic reaction energies and barriers is reported in Table C.4:

Reaction	Reaction energy <sup>IV</sup> ,	Reaction barrier <sup>V</sup> , eV
	eV	
$H_{2liq}+M_{cus} \leftrightarrow H_{2cus}$	-0.09 <sup>I</sup>	-
$H_{2cus} + O_{br} \leftrightarrow H_{cus} + OH_{br}$	+0.84	0.94
$H_{cus}+O_{br}\leftrightarrow OH_{br}+M_{cus}$	-0.81	1.22
$H_{cus}+OH_{br}\leftrightarrow H_2O_{br}+M_{cus}$	-0.38	1.26
$FA_{liq}+M_{cus} \leftrightarrow FA_{cus}$	-0.60 <sup>I</sup>	-
$FA_{cus}+O_{br}\leftrightarrow FAmH_{cus}+OH_{br}$	+0.03	_II
$2OH_{br} \leftrightarrow O_{br} + H_2O_{br}$	+0.43	0.81
$H_2O_{liq}+V_{br} \leftrightarrow H_2O_{br}$	-0.80 <sup>I</sup>	-
$FA_{liq} \leftrightarrow FA_{br}$	-0.88 <sup>I</sup>	-
$FA_{br} \leftrightarrow (MF+O)_{br}$	-1.44	$0.65^{III}$
$MF_{liq}\!\!+\!\!O_{br}\!\!\leftrightarrow\!\!(MF\!\!+\!\!O)_{br}$	-0.01 <sup>I</sup>	-

Table C.4. Reaction network implemented in the microkinetic model.

<sup>I</sup>Reaction energies are given with respect to H<sub>2</sub>O, FA, H<sub>2</sub>, and MF in a vacuum <sup>II</sup>The reaction is assumed equilibrated, as alcohol O-H scission products are known to appear already at sub-ambient temperatures<sup>220</sup>

<sup>III</sup>The C-O scission and C-H bond formation steps were combined in a single CINEB calculation; the minimal energy pathway is similar to the radical-mediated one we previously reported on  $\text{RuO}_2^8$ 

<sup>IV</sup>Calculated using the (2x2x1) k-point mesh

<sup>V</sup>Calculated using Γ-point Brillouin zone sampling

### C.4.2 Details of DFT Calculations

Details of DFT calculations (Table C.4) not presented in this subsection can be found in the main manuscript. We employed the PBE functional; no U corrections were added. All structures were calculated ensuring an even number of electrons (vide *infra*). In particular, OH<sub>br</sub> and H<sub>cus</sub>,+O<sub>br</sub> structures contained an extra H atom bound to O<sub>br</sub> in the neighboring row. Vibrational frequencies were calculated using the finite difference method, with the electronic loop tolerance set to  $10^{-6}$  eV. 1-2 imaginary frequencies present for certain weakly bound species (adsorbed furfuryl alcohol and 2methyl furan) were neglected. Reaction barriers were calculated using a combination of nudged elastic band (NEB) and the climbing-Image NEB methods.<sup>57,58,60</sup> 10 images were utilized in optimizations. The Brillouin zone was sampled in the  $\Gamma$ -point (initial states were recalculated at the  $\Gamma$ -point for the purpose of barrier calculations). The force convergence criterion was set to 0.1 eV/Å. Vibrational energy and entropy contributions to reaction barriers were neglected (i.e. vibrational energy and entropy of transition and initial states were assumed to be equal). From our experience, this is a reasonable assumption for covalently bound species on catalyst surfaces. In calculations of adsorption equilibrium constants, we assume that the bulk and surface phases are energetically decoupled, i.e. the liquid solvent does not modify surface species energetics directly. This is a realistic approximation due to a low dielectric constant of toluene (2.38) and no charged species involved.

In our prior  $RuO_2(110)$  calculations, we found that relaxing the top stoichiometric slab layer is sufficient to obtain converged energetics. However, this is not the case for TiO<sub>2</sub>(110). Table C.5 displays the significant difference between 1relaxed layer and 3-relaxed layer calculations for species absolute energies. In addition, in Figure C.4 we illustrate the effect of slab relaxations on average binding energies of hydrogen, adsorbed on  $O_{br}$  sites at varying coverages, calculated relative to the H<sub>2</sub> experimental chemical potential. Due to the substantial effect of relaxations, we employ the TiO<sub>2</sub>(110) slab with 3 relaxed top layers in all of our subsequent calculations, including those reported in Table C.4 and in the main manuscript.



Table C.5. Effect of slab relaxations on species energetics

Figure C.4. Effect of slab relaxations on lateral interactions and surface termination.

### C.4.3 New Energy Referencing Scheme

In microkinetic models used in catalysis, especially in metal catalysis, electronic formation energies of surface species are calculated from the following:

$$\Delta E_{form} = E_{A/S} - E_S - \sum_i \nu_i E_{i,ref} \tag{C.10}$$

Here  $E_{A/S}$  is the DFT energy of an adsorbate on top of a metal or metal oxide slab S;  $E_S$  is the DFT energy of a clean slab;  $E_{i,ref}$  are the energies of reference gas phase species;  $v_i$  are the corresponding stoichiometric coefficients. As the A component in A/S is often coordinatively unsaturated when it is not bound to the metal, the A/S may contain an odd number of electrons. The electron number parity does not play a role in calculations for adsorbates on metals due to delocalization, and so direct reaction energy calculations involving coadsorbed, well-separated reactants and products, vs. indirect calculations with species on separate slabs (equation C.10) yield almost identical results. This is not the case for semiconductors and insulators, such as metal oxides. To illustrate this, we compare direct reaction energy calculations with indirect ones using 3 different reference slab and species environment choices on  $TiO_2(110)$ . Three sets of references are depicted in Figure C.5. In set (A), we used the same reference for all species, as it is commonly done in microkinetic models on metal catalysts. In (B), the pristine  $TiO_2(110)$  was used as a reference for  $H_{cus}$  and  $H_{2cus}$  as the most representative catalyst structure under reaction conditions, since the vacancy coverage is typically very low. In set (C), species with an even number of electrons were employed, whereas references contained either even or odd numbers of electrons.

(7	4)			(B)
Species	Reference		Species	Reference
H <sub>2,cus</sub> +O <sub>br</sub>	$TiO_{2,vac}$		$H_{2,cus}$	TiO <sub>2</sub>
$H_{cus}$	$TiO_{2,vac}$		$H_{cus}$	TiO <sub>2</sub>
$O_{br}$	$TiO_{2,vac}$		$O_{br}$	TiO <sub>2,vac</sub>
$OH_{br}$	$TiO_{2,vac}$		$OH_{br}$	$TiO_{2,vac}$
$H_2O_{br}$	$TiO_{2,vac}$		$H_2O_{br}$	TiO <sub>2,vac</sub>
$FCH_2OH_{br}$	$TiO_{2,vac}$		$\rm FCH_2OH_{br}$	TiO <sub>2,vac</sub>
FCH <sub>3,br</sub>	$TiO_{2,vac}$		$FCH_{3,br}$	TiO <sub>2,vac</sub>
		(C)		
	Species	R	eference	-
	H <sub>2,cus</sub>		TiO <sub>2</sub>	
	$H_{cus}$	TiO	O <sub>2,vac</sub> +OH <sub>br</sub>	
	O <sub>br</sub>		TiO <sub>2,vac</sub>	
	$OH_{br}$	Ti	$O_{2,vac}$ + $H_{br}$	
	$H_2O_{br}$		TiO <sub>2,vac</sub>	
	FCH <sub>2</sub> OH <sub>b</sub>	r	TiO <sub>2,vac</sub>	
	FCH <sub>3,br</sub>		TiO <sub>2,vac</sub>	

Figure C.5. Three sets of references considered in energy calculations.

In Table C.6, we report errors associated with referencing schemes. It is evident that no scheme provides satisfactory results for reaction energetics, and there is a need for an alternative referencing approach.

	Reaction energies, eV (errors due to referencing are given in parentheses)			
Reaction	Direct	Scheme A	Scheme B	Scheme C
	from DFT			
$H_{2,cus}+O_{br}\rightarrow H_{cus}+OH_{br}$	+0.41	+0.18 (-0.23)	+1.65 (+1.24)	+0.40 (-0.01)
$H_{cus}+O_{br}\rightarrow OH_{br}$	-1.44	-1.38 (+0.06)	-2.85 (-1.41)	-1.62 (-0.18)
Hcus+OHbr=H2Obr	-0.66	-0.43 (+0.23)	-1.89 (-1.23)	-0.65 (+0.01)
20Hbr=H2Obr+Obr	+0.78	+0.95	+0.95 (+0.17)	+0.97
		(+0.17)		(+0.19)
FCH <sub>2</sub> OH=FCH <sub>3</sub>	-0.74	-0.74	-0.74	-0.74
2OH <sub>br</sub> =2O <sub>br</sub> +H <sub>2</sub>	+1.11	+1.28	+1.28 (+0.17)	+1.30
		(+0.17)		(+0.19)

Table C.6. Effect of reference choice on reaction energy calculations

The sensitivity of reaction energetics reported in Table C.6 on the choice of the reference and the immediate reaction environment indicates that  $M_{cus}$  and  $V_{br}$  cannot be considered as independent sites, and their adsorbate energetics and thus occupancies are correlated. To account for such correlations, we combine two types of sites and define a single site, involving a pair of  $M_{cus}$  and  $V_{br}$ . We denote such site as c-V, where a sequence of symbols before the dash correspond to a  $M_{cus}$  site, and those after – to a  $V_{br}$  site. Due to combinatorics, 5  $M_{cus}$ -associated and 6  $V_{br}$  –associated species (see Section C.4.1) translate to 26 one-site species. Similarly, 9 unique reaction types translate to 9 equivalent reaction families, with the total number of reactions reaching 164. Reactions belonging to the same family describe an identical physical process, e.g., H migration from  $M_{cus}$  to  $O_{br}$  (H-O  $\rightarrow$ c-OH and c-O+H-O $\rightarrow$ c-OH+c-O). For such reactions, we assume identical electronic reaction energies.

Due to energy dependence on the electron number parity (Table C.6), we enforce parity conservation and only employ those DFT calculations that contain an even number of electrons. Since single-site MKM species formally contain either even (c-V, c-O,  $H_2$ -O) or odd number of electrons (H-O, O-H), we designed a two-step, indirect procedure to translate DFT energies to MKM. First, we define 6 "building blocks" and calculate their "intrinsic" energies from DFT using expressions described in Table C.7.

Tuble C.7. Dullang blocks	Table C.7.	"Building	blocks'
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Species	Mathematical expression for species energy
V <sub>br</sub>	Reference (energy set to 0)
Obr	$E[O_{br}] = E_{dft}[TiO_2(110)]^I - E_{dft}[TiO_2(110):V_{br}]^{II}$
H <sub>2cus</sub>	$E[H_{2,cus}] = E_{dft}[TiO_2(110):H_{2cus}]^{III} - E_{dft}[TiO_2(110)]$
$H_2O_{br}$	$E[H_2O_{br}] = E_{dft}[TiO_2(110): H_2O_{br}]^{IV} - E_{dft}[TiO_2(110): V_{br}]$
FA <sub>br</sub>	$E[FA_{br}] = E_{dft}[TiO_2(110):FA_{br}]^V - E_{dft}[TiO_2(110):V_{br}]$
FAcus	$E[FA_{cus}] = E_{dft}[TiO_2(110): FA_{cus}]^{VI} - E_{dft}[TiO_2(110)]$

 $I - TiO_2(110)$  slab; II – slab with a vacancy; III – H<sub>2</sub> adsorbed on a M<sub>cus</sub> site of the slab; IV – H<sub>2</sub>O adsorbed on a V<sub>br</sub> site; V – furfuryl alcohol adsorbed on a V<sub>br</sub> site; VI – furfuryl alcohol adsorbed on a M<sub>cus</sub> site.

In the next step, we compute energies of one-site MKM species using combinations of DFT-based electronic reaction energies, reported in Table C.4. Calculation details are presented in Table C.8.

Species	Chemical reaction employed	Mathematical expression for
		energy
c-O	-	$E[c-O] = E[O_{br}]$
H <sub>2</sub> -O	-	$E[H_2-O] = E[O_{br}] + E[H_{2,cus}]$
FA-O	-	$E[FA-O] = E[O_{br}] +$
		$E[FA_{cus}]$
c-V	-	E[c-V] = 0
H <sub>2</sub> -V	-	$E[H_2-V] = E[H_{2,cus}]$
FA-V		$E[FA-V] = E[FA_{cus}]$
H-OH	H <sub>2cus</sub> +O <sub>br</sub> =H <sub>cus</sub> +OH <sub>br</sub>	$E[\text{H-OH}] = E[\text{H}_2\text{-O}] + E_{\text{rxn}}$
FAmH-OH	FAcus+Obr=FAmHcus+OHbr	E[FAmH-OH] = E[FA-
		$O]+E_{rxn}$
c-H <sub>2</sub> O	-	$E[c-H_2O] = E[H_2O_{br}]$
H <sub>2</sub> -H <sub>2</sub> O	-	$E[H_2-H_2O] = E[H_{2,cus}] + E[c-$
		H <sub>2</sub> O]
FA-H <sub>2</sub> O	-	$E[H_2-H_2O] = E[FA_{cus}] + E[c-$
		H <sub>2</sub> O]
c-FA	-	$E[c-FA] = E[FA_{br}]$
H <sub>2</sub> -FA	-	$E[H_2-FA] = E[H_{2.cus}] + E[c-$
		FA]
c-MF	FA <sub>br</sub> =(MF+O) <sub>br</sub>	$E[c-MF] = E[c-FA] + E_{rxn}$
H <sub>2</sub> -MF	FA <sub>br</sub> =(MF+O) <sub>br</sub>	$E[H_2-MF] = E[H_2-FA]+E_{rxn}$
c-OH	H <sub>cus</sub> +O <sub>br</sub> =OH <sub>br</sub> +M <sub>cus</sub>	E[c-OH] = (E[c-O] + E[H-OH])
		$+E_{rxn})/2$
FAmH-V	-	E[FAmH-V] = E[FAmH-OH]-
		E[c-OH]
H-V	-	$E[\text{H-V}] = E[\text{H-O}] - E[O_{br}]$
FAmH-O	-	E[FAmH-O] = E[FAmH-V]+
		$E[O_{br}]$
H-O	H <sub>2cus</sub> +Obr=H <sub>cus</sub> +OH <sub>br</sub>	$E[\text{H-O}] = E[\text{H}_2\text{-O}] + E[\text{c-}$
		$O]+E_{rxn}-E[c-OH]$
H <sub>2</sub> -OH	-	$E[H_2-OH] = E[c-$
		OH]+ $E[H_{2,cus}]$
FA-OH	-	E[FA-OH] = E[c-
		$OH]+E[FA_{cus}]$
H-H <sub>2</sub> O	-	$E[H-H_2O] = E[H-$
		$V]+E[H_2O_{br}]$
FAmH-H <sub>2</sub> O	-	$E[FAmH-H_2O] = E[FAmH-$

Table C.8. Energy calculations for MKM species

		$V] + E[H_2O_{br}]$
H-FA	-	$E[\text{H-FA}] = E[\text{H-V}] + E[FA_{br}]$
H-MF	-	E[H-MF] = E[H-V] + E[c-MF]

When calculating the zero-point energy correction, temperature effects, and surface species entropy, we assume that vibrations of  $M_{cus}$ -associated and  $V_{br}$ -associated species are decoupled. This allows us to express non-electronic Gibbs free energy contributions of 26 surface species in terms of the following "vibrational building blocks" (Table C.9; frequencies are not reported here):

Table C.9. Vibrational frequencies for species employed in the MKM

Species	Slab structure used in	Relaxed
	frequency calculations	fragment
H <sub>cus</sub>	$TiO_2(110)$ : $H_{cus}$ , $OH_{br}$	H <sub>cus</sub>
H <sub>2cus</sub>	$TiO_{2}(110): H_{2cus}$	$H_{2cus}$
FA <sub>cus</sub>	$TiO_2(110)$ : $FA_{cus}$	FA <sub>cus</sub>
<b>FAmH</b> <sub>cus</sub>	$TiO_2(110)$ : $FAmH_{cus}$ , $OH_{br}$	FAmH <sub>cus</sub>
O <sub>br</sub>	$TiO_{2}(110)$	$O_{br}$
OH <sub>br</sub>	$TiO_2(110): OH_{br}, OH_{br}$	$OH_{br}$
$H_2O_{br}$	$TiO_{2}(110): H_{2}O_{br}$	$H_2O_{br}$
FA <sub>br</sub>	$TiO_{2}(110):FA_{br}$	$FA_{br}$
MF+O <sub>br</sub>	$TiO_2(110)$ : MF, $O_{br}$	$MF, O_{br}$

We accounted for dispersion interactions in adsorbed furanics by calculating the binding energy difference between PBE and PBE-D3 functionals, corrected by an estimate of erroneous D3 overbinding for covalent interactions. For example, the dispersion energy contribution for FA<sub>br</sub> was computed as  $\Delta E_{PBE-D3}(FA_{br}) - \Delta E_{PBE}(FA_{br}) - (\Delta E_{PBE-D3}(H_2O_{br}) - \Delta E_{PBE}(H_2O_{br}))$ , where  $\Delta E$  are species binding energies. To account for PBE errors in the description of covalent interactions, we computed the bulk  $TiO_2$  formation energy error per O atom (+0.17 eV) with respect to the experimental value and corrected DFT energies of species that lack Ti-O covalent bonds (a vacancy, a vacancy with adsorbed H<sub>2</sub>O or FA, etc.) by +0.17 eV.

It is important to note that the qualitative agreement of both reaction rates and reaction orders with experiment was only possible when both dispersion interactions and PBE-inherent errors were taken into account in MKM.

Comparison of experimental and MKM-predicted reaction orders is reported in Figure C.6.



Figure C.6. Comparison of predicted vs. experimental reaction orders with respect to furfuryl alcohol.

## C.5 Model of the C-O Bond Activation



Figure C.7. Kinetic model schematics.

The rate for 2-methyl furan (2MF) formation is:

$$r_{MF} = k_2 \theta_{vac} c_{FA} \tag{C.11}$$

Here  $\theta_{vac}$  is vacancy surface coverage and  $c_{FA}$  is the FA concentration in the bulk. If we apply pseudo-steady-state hypothesis for the vacancies, we obtain:

$$k_1\theta_0 p_{H_2} - k_{-1}\theta_{vac}c_{water} - k_2\theta_{vac}c_{FA} = 0 \tag{C.12}$$

Substituting the site balance  $\theta_0 = 1 - \theta_{vac}$  into (C.12),

$$k_1 p_{H_2} - k_1 \theta_{vac} p_{H_2} - k_{-1} \theta_{vac} c_{water} - k_2 \theta_{vac} c_{FA} = 0$$
(C.13)

Solving for  $\theta_{vac}$ ,

$$\theta_{vac} = \frac{k_1 p_{H_2}}{k_2 c_{FA} + k_{-1} c_{water} + k_1 p_{H_2}} \tag{C.14}$$

Substituting (C.14) into the  $r_{MF}$  expression (eq. C.11),

$$r_{MF} = \frac{k_2 k_1 p_{H_2}}{k_2 c_{FA} + k_{-1} c_{water} + k_1 p_{H_2}} c_{FA}$$
(C.15)

If reaction 2 is the rate-limiting step (RLS), then  $k_2 c_{FA} \ll k_{-1} c_{water} + k_1 p_{H_2}$ , and thus

$$r_{MF} = \frac{k_2 k_1 p_{H_2}}{k_{-1} c_{water} + k_1 p_{H_2}} c_{FA}$$
(C.16)

Therefore, FA reaction order is 1.

If reaction 1 (vacancy formation) is rate-determining (i.e.,  $k_2 c_{FA} \gg k_1 p_{H_2}$ ,  $k_2 c_{FA} \gg k_{-1} c_{water}$ ), then

$$r_{MF} = k_1 p_{H_2} \tag{C.17}$$

FA reaction order is 0.

Since the experimental FA reaction orders are in a range of 0.65-0.95, we conclude that the C-O scission being the RLS and vacancy formation being quasi-

equilibrated on all oxide materials we considered are consistent with the simple Langmuir-Hinshelwood analysis.

# C.6 Additional Data for Reactions, Calculations and Characterization



Figure C.8. Effect of the homolytic C-O bond cleavage energy on the HDO rate over oxides. 0.1 M alcohol in toluene, 160  $^{\circ}$ C, 12 bar H<sub>2</sub>.

Oxide	Surface	Hydrogen affinity**,	Optical band gap of
surface	termination*	eV	the bulk material, eV
ZnO (1010)	$1 \text{ ML H}_{O}, 1 \text{ ML H}_{M}$	-0.77	$3.3^{407}$
IrO <sub>2</sub> (110)		-0.66	
IrO <sub>2</sub> (101)	$1 \text{ ML H}_{O}, 1 \text{ ML H}_{M}$	-0.43	0
IrO <sub>2</sub> (100)		-0.57	
RuO <sub>2</sub> (110)		-0.50	
RuO <sub>2</sub> (101)		-0.04	0
RuO <sub>2</sub> (100)		-0.25	
SnO <sub>2</sub> (110)	1 ML H	-0.17	$3.4^{408}$
MoO <sub>3</sub> (100)	$1 \text{ IVIL } \Pi_0$	-0.31	$2.97^{409}$
$VO_2$		0.00	0
(110)***		-0.09	0
CeO <sub>2</sub> (111)		-0.88	$3.19^{410}$
$TiO_2(110)$	0.33 ML H <sub>0</sub>	-0.004	2 02222
TiO <sub>2</sub> (100)	Pristine	-	5.05

Table C.10. Calculated surface hydrogen affinities and experimental bulk optical band gaps for various oxides.

\* Notation corresponds to Figure 4 of the main text

\*\* Hydrogen affinity is calculated as the formation Gibbs free energy of the most thermodynamically stable hydrogenated surface per H atom, calculated relative to the pristine surface and the experimental H<sub>2</sub> chemical potential

\*\*\* For VO<sub>2</sub>, we consider metallic tetragonal (rutile) phase, stable above 340

K

Oxide surfaces	Type I	Type 2
	reaction	reaction
	energy, eV	energy, eV
CeO <sub>2</sub> (111)	2.31	-
TiO <sub>2</sub> (110)	1.55	2.52
TiO <sub>2</sub> (100)	1.98	-
VO <sub>2</sub> (110)	0.91	1.78
SnO <sub>2</sub> (110)	0.64	0.78
MoO <sub>3</sub> (100)	0.33	0.94
RuO2(110)	1.62	0.91
RuO2(101)	1.72	1.00
RuO2(100)	1.60	0.77
IrO <sub>2</sub> (110)	1.91	0.14
IrO <sub>2</sub> (101)	2.76	0.20
IrO <sub>2</sub> (100)	1.86	0.33

Table C.11. Comparison of calculated Type I and Type II reaction energies of vacancy formation (see the main text) relative to gas phase species and a surface vacancy. Calculations were carried out on thermodynamically optimal surfaces while maintaining an even number of electrons in all calculated structures

Molecule	Reaction	Bond Energy (eV)
Benzhydrol	OH	3.24
	+ он•	
4-	OH I	3.63
methylbenzy l alcohol	+ он•	
Cinnamyl alcohol	он + он.	3.31
Furfuryl alcohol		3.40

Table C.12. Electronic C-O bond dissociation energy of aromatic alcohols
## Appendix D

## MECHANISMS FOR HIGH SELECTIVITY IN HYDRODEOXYGENATION OF 5-HMF OVER PTCO NANOCRYSTALS

Table D.1. Comparison of estimated properties of three  $Pt_3Co_2$  NCs: an alloy core/surface  $Co_3O_2$  monolayer shell geometry, a  $Pt_3Co_2$  random alloy, and a Pt NC of the same size.

		Pt <sub>3</sub> Co <sub>2</sub> (core/shell)	Pt <sub>3</sub> Co <sub>2</sub> (random allov)	Pt
Nanoparticle size		3.7 nm	3.7 nm	3.7 nm
Lattice constant		$3.87 \text{ Å}^1$	$3.77 \text{ Å}^2$	3.92 Å
Bulk Co fraction		14.4 %	40 %	-
Total number of atoms		1827	1983	1754
Number of surface atoms		662 (546 <sup>5</sup> )	700	645
Number of subsurface atoms		524	_3	_3
Dispersion		36.3 %	35.3 %	36.8 %
Distribution	Surface	74.8 % <sup>5</sup>	35.3 %	-
of Co atoms	Subsurface	10.3 % <sup>5</sup>	_3	-
in each part	Bulk	14.9 % <sup>5</sup>	64.7 %	-
	Surface	$0\%^{5}$	35.3 %	36.8 %
Distribution of Pt atoms in each part	Subsurface (under terraces)	22.8 % <sup>5</sup>	_3	_3
	Subsurface (under steps)	18.1 % <sup>5</sup>		
	Bulk	59.1 % <sup>5</sup>	64.7 %	63.2 %
Coordination numbers <sup>4</sup>	Pt-Co	2.92	4.38	-
	Pt-Pt	8.91	6.57	10.90
	Pt-M	11.83	10.94	10.90

<sup>1</sup>Calculated based on XRD; <sup>2</sup>estimated based on the bulk composition and Vegard's law; <sup>3</sup>subsurface atoms are considered part of the bulk, due to identical coordination; <sup>4</sup>for the  $Pt_3Co_2$  random alloy and the Pt NC,  $CN_{total} = 9$  in the surface and  $CN_{total} = 12$  in the bulk; <sup>5</sup>Assuming 70% of surface sites are present as a  $Co_3O_2$  honeycomb structure

Depation	#	DFT reaction	DFT reaction	
Reaction		energy, eV	barrier, eV	
Hydrogen activation				
$H_2 + * = H_2 *$	-	-0.14	N/A	
$H_2$ *= $H_{Pt-Co}$ *- $H_{Pt-Co}$ *	1	-0.15	0.68	
$H_2 *= H_{Pt-Co} *-OH_{vac} *$	2	-0.41	1.19	
$H_2$ *=2O $H_{vac}$ *	3	-0.86	1.5	
Vacancy formation				
$H_{Pt-Co}*-H_{Pt-Co}*=H_{Pt-Co}*-$	1	0.20	1 26	
OH <sub>vac</sub> *	4	-0.29	1.20	
HPt-Co*-OHvac*=H2Ovac*	5	+0.13	1.15	
$H_2O_{vac}$ *= $H_2O$ +* <sub>vac</sub>	-	+0.56	N/A	
HMF-to-HMMF conversion				
$HMF + 2H_{Pt-Co}* = HMF-2H_{Pt-}$		0.80	NI/A	
Co*	-	-0.80	1N/A	
$HMF-2H_{Pt-Co}^* = BHMF^*$	6	-0.56	0.84	
$BHMF^* = BHMF + *$	-	+0.91	N/A	
$BHMF^* = BHMFmOH^*$ -	7	0.02	1 10	
OH*	1	$\pm 0.93$	1.17	
BHMFmOH*-	0	0.10	0.17	
OH*=HMMF*-O*	0	-0.19	0.17	
$HMMF^*-O^* = HMMF + O^*$	-	+0.78	N/A	
O removal				
$H_2 + O^* = H_2^* - O^*$	-	-0.12	N/A	
$H_2^*-O^* = H_{Pt}^*-OH^*$	9	-1.21	$0.28^{1}$	
$H_{Pt}^*\text{-}OH^* = H_2O^*$	10	-0.90	0.23	
$H_2O^* = H_2O + *$	-	+0.41	N/A	
BHMF-to-HMMF conversion on a vacancy				
$BHMF + *_{vac} = BHMF*_{vac}$	-	-1.32	N/A	
BHMF vac* = BHMFmOH*-	11	⊥0 10	N/A	
OH <sub>vac</sub> *	11	T0.10	1 N/ A	
BHMFmOH*-	12	-0.63	N/A	
OH <sub>vac</sub> *=HMMF*	12	-0.03	11/21	
HMMF* = HMMF + *	-	+0.63	N/A	

Table D.2. DFT reaction energies and barriers on a  $Co_3O_2/Pt(111)$  honeycomb surface. Index numbers correspond to structures in Figure D.1.

\* – intact honeycomb oxide surface;

 $H_{Pt-Co}^*$  – hydrogen atom bound to Pt and Co atoms in a bridging configuration;  $OH_{vac}^*$  and  $H_2O_{vac}^*$  – OH and  $H_2O$  adsorbed on a vacancy;

O\*, OH\*, and H<sub>2</sub>O\* - O, OH, and H<sub>2</sub>O adsorbed on an intact honeycomb surface between two Co atoms in a bridging configuration; \*<sub>vac</sub> – honeycomb oxide with a vacancy; H<sub>2</sub>\*-O\* – O\* species with a H<sub>2</sub> molecule physisorbed nearby over a Pt atom HMF – 5-(hydroxymethyl)furfural; HMF-2H<sub>Pt-Co</sub>\* – HMF co-adsorbed with two H<sub>Pt-Co</sub>\* atoms; BHMF – 2,5-bis(hydroxymethyl)furan; BHMFmOH\* - radical formed after removal of the hydroxyl side group from BHMF; HMMF – 2-(hydroxymethyl)-5-methylfuran;

N/A – reaction barrier was not calculated

<sup>1</sup>Forces were converged at 0.2 eV/Å level due to slow convergence

Table D.3. Comparison of properties and numbers of surface atoms in  $Pt_3Co_2$  and  $Pt_3Co$  NCs with a core/shell structure.

	Pt <sub>3</sub> Co <sub>2</sub> (core/shell)	Pt <sub>3</sub> Co (core/shell)
Nanoparticle size	3.7 nm	3.2 nm
Lattice constant	3.87 Å <sup>1</sup>	$3.87 \text{ Å}^1$
Bulk Co fraction	14.4 %	$14.4 \%^2$
Total number of atoms	1827	1168
Number of surface atoms	662 <sup>3</sup>	491 <sup>3</sup>
Number of surface Co atoms	547 <sup>4</sup>	405 <sup>4</sup>
Number of surface Co atoms available at given bulk Co fraction	547	184

 $^{1}$ Calculated from XRD;  $^{2}$ Assumed to be the same as for Pt<sub>3</sub>Co<sub>2</sub>;  $^{3}$ Calculated for a close-packed surface;  $^{4}$ Based on 70% of Co<sub>3</sub>O<sub>2</sub>-covered terrace sites and 30% of CoO-covered steps

	250 °C, 1 bar	160 °C, 33 bar
	$H_2$	$H_2$
$\Delta G_{H_2,ads}$ , J/mol	$3.31 \cdot 10^4$	$2.16 \cdot 10^4 *$
$\Delta G_{0+H\to 0H}^{\neq}$ , J/mol	$1.17 \cdot 10^5$	$1.17 \cdot 10^5$
$\theta_{2H}$	$4.95 \cdot 10^{-4}$	8.19·10 <sup>-2</sup>
$k_{O+H\to OH}$ , s <sup>-1</sup>	$2.32 \cdot 10^{1}$	$6.42 \cdot 10^{-2}$
$r, s^{-1}$	1.15·10 <sup>-2</sup>	<b>5.26·10</b> <sup>-3</sup>

Table D.4. Calculation of the vacancy formation rate at conditions of kinetic measurements (160°C, 33 bar H<sub>2</sub>) and catalyst pretreatment/XAS conditions (250°C, 1 bar H<sub>2</sub>).

\*Gibbs free energy of reaction is given at 1 atm.



Figure D.1. Optimized structures of initial, transition, and final states that correspond to reactions in Table D.2. Blue atoms - Pt, orange atoms - Co, red atoms - oxygen, brown atoms - carbon. The figure continues on the next page.

HMF-to-BHMF conversion













8)

9)

10)

12)

O removal





MA

 $\Delta \Delta$ 





0















N/A







Figure D.2. Energy diagram for vacancy formation. Notations correspond to Table D.2.

# D.1 Relative Kinetic Stability Estimation of Co<sub>3</sub>O<sub>2</sub> Monolayer at 250 °C, 1 atm H<sub>2</sub> vs. 160 °C, 33 atm H<sub>2</sub>

We calculate the vacancy formation rate as

$$r = k_{0+H \to 0H} \theta_{2H} \tag{D.1}$$

Here  $k_{0+H\to 0H}$  is the rate constant for the OH formation reaction;  $\theta_{2H}$  is the surface coverage of dissociated H<sub>2</sub> molecules. The coverage is found assuming equilibrium between the chemical potentials of an adsorbed state, gaseous H<sub>2</sub> and vacant surface sites ( $\mu_{2H}$ ,  $\mu_{H_2,gas}$ , and  $\mu_*$ , respectively):

$$\mu_{2H} = \mu_{H_2,gas} + \mu_* \tag{D.2}$$

The chemical potentials are expressed in terms of surface coverages and  $H_2$  pressure:

$$\mu_{2H}^{0} + RT \ln \theta_{2H} = \mu_{H_2,gas}^{0} + RT \ln \frac{P_{H_2,bar}}{1 \ bar} + \mu_*^{0} + RT \ln \theta_*$$
(D.3)

Here a naught in a superscript denotes quantities at a given temperature (160 or 250 °C) and 1 bar H<sub>2</sub> pressure. The coverage of 2H species is calculated in terms of Gibbs free energy of adsorption  $\Delta G_{H_2,ads}$ , assuming  $\theta_* = 1$ , as

$$\theta_{2H} = exp\left(-\frac{\Delta G_{H_2,ads}}{RT}\right) \times \frac{P_{H_2,bar}}{1 \ bar} \tag{D.4}$$

The reaction rate constant is calculated according to the transition state theory:

$$k_{O+H\to OH} = \frac{k_B T}{h} exp\left(-\frac{\Delta G_{O+H\to OH}^{\neq}}{RT}\right)$$
(D.5)

Zero point energies and temperature corrections were accounted for in Gibbs free energy calculations by assuming that all surface species only possess vibrational degrees of freedom.

Following homolytic splitting of the H<sub>2</sub> molecule, one H atom transfers to a neighboring O atom to form OH (1.3 eV barrier). A second H atom attacks OH and produces water (1.2 eV barrier), which subsequently desorbs. The transition state of hydroxyl formation, O+H $\rightarrow$ OH, is the least stable (Figure D.2), suggesting OH formation to be the rate-limiting step of a vacancy formation. We find its rate at 160 °C and 33 bar H<sub>2</sub> to be equal to 5.26 · 10<sup>-3</sup> s<sup>-1</sup> (Table D.4), assuming the catalyst is in equilibrium with the H<sub>2</sub> gas. Under *in situ* XAS conditions (250 °C and 1 bar H<sub>2</sub>), the corresponding vacancy formation rate is greater by a factor of two (1.15 · 10<sup>-2</sup> s<sup>-1</sup>). Once formed, the vacancy is easily reoxidized by BHMF-to-HMMF reactions (Table D.2, reactions 11-12) with a rate of 4 · 10<sup>10</sup> s<sup>-1</sup> (0.2 eV C-O scission barrier). This analysis

provides a rationalization as to why the  $Co_3O_2$  surface oxide is stable in a reducing reaction environment.

Appendix E

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